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FOR

CHEMICAL STUDENTS.

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LECTURE NOTES

FOR

CHEMICAL STUDENTS.

VOL. II.
ORGANIC CHEMISTRY.

BY

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THIRD EDITION.
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PREFACE TO THE THIRD EDITION.

WHILST the rapid progress of organic chemistry has on the one hand enormously increased the number of organic compounds, it has, on the other, revealed new relations between the different groups of these compounds and opened up many new paths, both from one group to another and from member to member of the same group. The relative importance of individual compounds has thus gradually diminished in comparison with that of the family to which they belong; and this condition of things can only be fully recognised by so classifying organic bodies as to make the description of the individual members subsidiary to that of the family to which they are attached. The student is thus enabled to gain a general view of the otherwise almost hopelessly vast array of organic substances.

These principles, enunciated in the first edition of this work, have been adhered to in the present edition, which has been carefully revised and brought down to date by Dr. F. R. Japp. The chapters on benzene and the benzene theory, on naphthalene, phenanthrene, anthracene, and the indigo group, are from his pen.

Baeyer's new synthesis of indigo, which was made known while this work was in the press, is given in an appendix.

ROYAL COLLEGE OF CHEMISTRY,
SOUTH KENSINGTON MUSEUM,
3rd January, 1881.

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ERRATUM.

Page 138, line 15 from top, *for* "$C_nH_{2n+1}Ho$" *read* "$C_nH_{2n-1}Ho$."

LECTURE NOTES

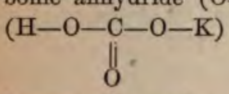
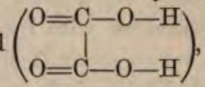
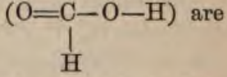
FOR

CHEMICAL STUDENTS.

ORGANIC CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

THE name *organic* is conveniently restricted to chemical compounds the molecules of which consist of one or more atoms of carbon *directly* combined either with carbon, nitrogen, or hydrogen. Thus, according to this definition, carbonic anhydride ($O{=}C{=}O$) and hydric potassic carbonate  $(\mathrm{H{-}O{-}\underset{\substack{\| \\ O}}{C}{-}O{-}K})$ are inorganic or mineral compounds, because the carbon which they contain is directly combined with oxygen only; but oxalic acid  $\left(\begin{array}{c}\mathrm{O{=}C{-}O{-}H}\\ |\\ \mathrm{O{=}C{-}O{-}H}\end{array}\right)$, cyanic acid ($N{\equiv}C{-}O{-}H$), and formic acid  $(\mathrm{O{=}\underset{\substack{| \\ H}}{C}{-}O{-}H})$ are organic compounds, because their molecules contain carbon directly combined, in the first case with carbon, in the second with nitrogen, and in the third with hydrogen.

The number of elements usually entering into the composition of organic compounds is very small.

A large number of these compounds consist of carbon united with only *one* other element, either hydrogen or, rarely, nitrogen.

The members of another very large class contain only *three* elements :—carbon, hydrogen, and oxygen ; carbon, hydrogen, and nitrogen ; or carbon, nitrogen, and oxygen.

Others contain *four* elements—carbon, hydrogen, oxygen, and nitrogen.

Some contain sulphur, chlorine, bromine, iodine, silicon, phosphorus, boron, or metals ; but these are comparatively rare.

Although the number of the elements entering into the composition of organic compounds is much smaller than that usually taking part in the formation of minerals, yet the complexity of the former class of compounds is frequently much greater.

There is no instance of an organic molecule containing but two single atoms, and only one in which there are three (hydrocyanic acid, HCN).

On the other hand, the number of atoms in a single organic molecule is sometimes very great. Thus :—

The molecule of Spermaceti contains 98 atoms.
" " Stearin " 173 "
" " Margarin " 217 "

In nearly all organic compounds *carbon is a tetrad.* It forms, therefore, with 1 atom of hydrogen a triad compound radical, which exists in chloroform $(\mathbf{C}^{iv}H)'''Cl_3$; a dyad compound radical with 2 atoms of hydrogen, as in methylenic dichloride $(\mathbf{C}^{iv}H_2)''Cl_2$; and a monad compound radical with 3 atoms of hydrogen, as in methylic iodide $(\mathbf{C}^{iv}H_3)I$. But in these compounds it will be seen that the carbon is always saturated and always a tetrad.

This is in conformity with the following general law :—"In every molecule of a chemical compound the sum of the bonds is always an even number," because every number, whether odd or even, when multiplied by 2 gives an even number. To this may be added the following law, to which no exception is known:—"The sum of the bonds in any molecule is at least twice as great as the active atomicity of the most polyad element in the compound."

A compound organic radical is a group of atoms containing one or more atoms of carbon of which one or more bonds are unsatisfied; and it is either a monad, dyad, &c. radical, according to the number of monad atoms required to complete its active atomicity.

Such a radical, when a monad, triad, or pentad, cannot exist as a separate group; like hydrogen or nitrogen, when isolated, it combines with another group of atoms like itself, forming a duplex molecule. It is only by this union of two semi-molecules that the vacated bonds can be satisfied.

The following are two of the principal series of compound organic radicals:—

Monads.		Dyads.	
Methyl..	$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_3\end{matrix}\right.$ or $\left\{\begin{matrix}\mathrm{Me}\\ \mathrm{Me}\end{matrix}\right.$	Methylene..	$\mathbf{C}H_2$ or Me″*.
Ethyl ..	$\left\{\begin{matrix}\mathbf{C}_2H_5\\ \mathbf{C}_2H_5\end{matrix}\right.$ or $\left\{\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\right.$	Ethylene ..	$\mathbf{C}_2H_4$ or Et″.
Propyl..	$\left\{\begin{matrix}\mathbf{C}_3H_7\\ \mathbf{C}_3H_7\end{matrix}\right.$ or $\left\{\begin{matrix}\mathrm{Pr}\\ \mathrm{Pr}\end{matrix}\right.$	Propylene..	$\mathbf{C}_3H_6$ or Pr″.
Butyl ..	$\left\{\begin{matrix}\mathbf{C}_4H_9\\ \mathbf{C}_4H_9\end{matrix}\right.$ or $\left\{\begin{matrix}\mathrm{Bu}\\ \mathrm{Bu}\end{matrix}\right.$	Butylene ..	$\mathbf{C}_4H_8$ or Bu″.
Amyl ..	$\left\{\begin{matrix}\mathbf{C}_5H_{11}\\ \mathbf{C}_5H_{11}\end{matrix}\right.$ or $\left\{\begin{matrix}\mathrm{Ay}\\ \mathrm{Ay}\end{matrix}\right.$	Amylene ..	$\mathbf{C}_5H_{10}$ or Ay″.

Organic radicals are the analogues of the monad, dyad, and triad elements of mineral chemistry.

Such being the constitution of the organic radicals, let us now proceed to investigate their functions in organic compounds, and to examine the general plan upon which these compounds are, on the atomic hypothesis, built up.

We shall be assisted in our investigation by reducing the formulæ of these compounds to a few types or fundamental forms. In doing this it is necessary to avoid, as far as possible, all empirical grouping of atoms. Our formulæ ought to express, as exactly as possible, how the elements are combined with each other. Thus in a compound containing $C_xH_yO_z$, the formula ought to show, first, whether the hydrogen is combined with carbon or with oxygen; or if combined with both, it should indicate how many atoms are united with carbon, and how many with oxygen. Secondly, the formula ought to show whether the oxygen is united with carbon or with hydrogen, or partly with the one and partly with the other, or, lastly, whether it is performing the function of linking hydrogen to carbon.

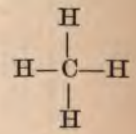
---

* Only known in combination.

This information is most completely given, in notation, by making carbon the dominant or grouping element in non-nitrogenous compounds, and nitrogen in the remaining organic compounds.

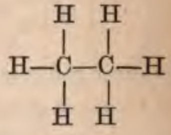
Non-nitrogenous organic compounds, exclusive of organo-metallic bodies and organo-boron and silicon compounds, can be conveniently considered under the two following types, viz.:—

1. The monadelphic, or marsh-gas type ....



$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H}$$

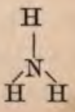
2. The diadelphic, or methyl type ..



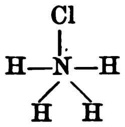
$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H}$$

Nitrogenous organic compounds arrange themselves in the most convenient manner under the two following types:—

3. The ammonia type ....

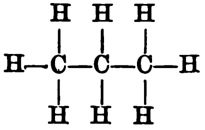


4. The ammonic-chloride type......



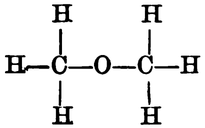
In addition to these types a few others will be occasionally necessary, such as:—

5. The triadelphic type............



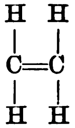
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

6. The double monadelphic type....



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

7. The condensed diadelphic or olefine type ....



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

Double, and sometimes even treble ammonia and ammonic-chloride types are required for certain compounds, but they do not need special description here.

The above types are written symbolically as follows: —

1. Monadelphic type	CH_4.
2. Diadelphic type	$\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$.
3. Ammonia type................	$N'''H_3$.
4. Ammonic-chloride type	N^vH_4Cl.
5. Triadelphic type	$\left\{\begin{matrix}CH_3\\CH_2\\CH_3\end{matrix}\right.$.
6. Double monadelphic type	$\left\{\begin{matrix}CH_3\\O\\CH_3\end{matrix}\right.$.
7. Condensed diadelphic type	$''\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.$.

In order to facilitate the use of these symbolic types, it is advisable for the student to become familiarized with the symbols of the following analogues of hydroxyl, in addition to those already given for inorganic compound radicals at p. 28 of vol. i, and for the monad and dyad radicals at p. 3 of the present volume:—

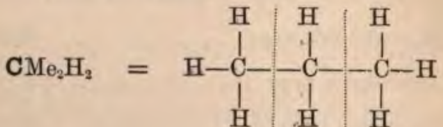
Methoxyl	$\mathbf{C}H_3O$	or Meo.
Ethoxyl	$\mathbf{C}_2H_5O$	or Eto.
Propoxyl	$\mathbf{C}_3H_7O$	or Pro.
Butoxyl	$\mathbf{C}_4H_9O$	or Buo.
Amoxyl	$\mathbf{C}_5H_{11}O$	or Ayo.

Formulæ written on the triadelphic type can be reduced to the diadelphic type, and those on the latter to the monadelphic type, as follows:—

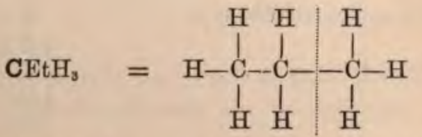
$$\begin{array}{c}\text{Propylic}\\\text{hydride}\end{array}\left\{\begin{array}{l}\mathbf{C}H_3\\\mathbf{C}H_2\\\mathbf{C}H_3\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}MeH_2\\\mathbf{C}H_3\end{array}\right. = \mathbf{C}Me_2H_2 \text{ or } \mathbf{C}EtH_3.$$

Triadelphic. Diadelphic. Monadelphic.

The above alternative monadelphic formulæ, although apparently different, are in reality identical, as can be easily proved by expressing both graphically, thus:—



$$\mathbf{C}Me_2H_2 = \begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -H \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$



$$\mathbf{C}EtH_3 = \begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -H \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$

On the other hand, monadelphic formulæ, if they contain a sufficient number of carbon atoms, can be expanded into diadelphic, triadelphic, &c., formulæ in the following manner:—

$$\mathbf{C}BuPrH_2 = \left\{\begin{array}{l}\mathbf{C}PrH_2\\ \mathbf{C}PrH_2\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}EtH_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}EtH_2\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}MeH_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}MeH_2\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_3\end{array}\right..$$

Normal butyl, or propylated methyl. (Molecule.)

This development of normal butyl depends on the following facts:—1st, that normal butyl is propylated methyl; 2nd, that normal propyl is ethylated methyl; and 3rd, that ethyl is methylated methyl.

Secondary and tertiary organic radicals (see p. 10) cannot be completely developed vertically:—

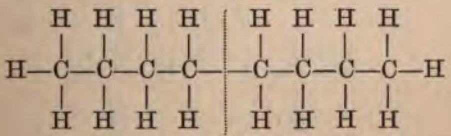
$$\left\{\begin{array}{l}\mathbf{C}EtMeH\\ \mathbf{C}EtMeH\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}MeH_2\\ \mathbf{C}MeH\\ \mathbf{C}MeH\\ \mathbf{C}MeH_2\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2\\ \mathbf{C}MeH\\ \mathbf{C}MeH\\ \mathbf{C}H_2\\ \mathbf{C}H_3\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2\\ \mathbf{C}H(CH_3)\\ \mathbf{C}H(CH_3)\\ \mathbf{C}H_2\\ \mathbf{C}H_3\end{array}\right.:$$

Methylo-ethylated methyl. (Molecule.)

$$\left\{\begin{array}{l}\mathbf{C}Me_3\\ \mathbf{C}Me_3\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}Me_2\\ \mathbf{C}Me_2\\ \mathbf{C}H_3\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}(CH_3)(CH_3)\\ \mathbf{C}(CH_3)(CH_3)\\ \mathbf{C}H_3\end{array}\right..$$

Trimethylated methyl. (Molecule.)

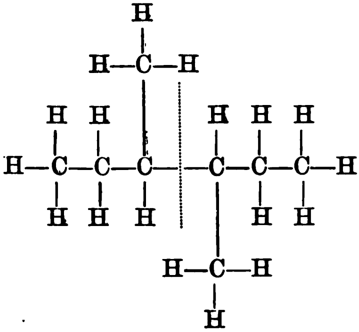
It will be seen, on comparing the above formulæ with the graphic representation of the respective compounds, that both express the same ideas of constitution. Thus in the developed symbolic formula of normal butyl it is evident that the two extreme carbon atoms are each united with three atoms of hydrogen and one of carbon, and all the intermediate carbon atoms with two of hydrogen and two of carbon, exactly as shown in the following graphic representation:—



$$\begin{array}{cccccccccccccccccc} & & H & & H & & H & & H & & H & & H & & H & & H & \\ & & | & & | & & | & & | & & | & & | & & | & & | & \\ H & — & C & — & C & — & C & — & C & — & C & — & C & — & C & — & C & — H\\ & & | & & | & & | & & | & & | & & | & & | & & | & \\ & & H & & H & & H & & H & & H & & H & & H & & H & \end{array}$$

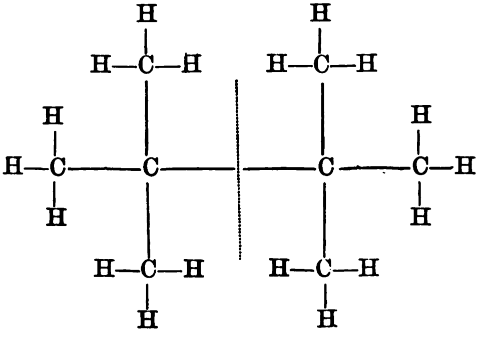
Normal butyl or propylated methyl. (Molecule.)

From the developed symbolic formula of methylo-ethylated methyl, it is evident that the two central carbon atoms are united with three atoms of carbon and one of hydrogen, that the two extreme carbon atoms are united with one atom of carbon and three of hydrogen, that the intermediate carbon atoms are joined to two hydrogen and two carbon atoms, and that the remaining carbon atoms are each combined with one atom of carbon, and three of hydrogen, thus:—



Methylo-ethylated methyl. (Molecule.)

Lastly, in the developed symbolic formula for trimethylated methyl, the two central atoms of carbon are each united with four carbon atoms, and all the remaining atoms of carbon are united with three of hydrogen and one of carbon, thus:—



Trimethylated methyl. (Molecule.)

CLASSIFICATION OF ORGANIC COMPOUNDS.

The most important organic compounds can be conveniently divided into the following thirteen families :—

1. Organic radicals.
2. Hydrides of organic radicals.
3. Alcohols.
4. Ethers.
5. Haloid ethers.
6. Aldehydes.
7. Acids.
8. Anhydrides.
9. Ketones.
10. Ethereal salts.
11. Organic compounds containing triad or pentad nitrogen.
12. Organo-boron and silicon compounds.
13. Organo-metallic bodies.

CHAPTER II.

ORGANIC RADICALS.

This family of organic compounds is divided into two classes :—

Class I. Positive radicals.
Class II. Negative radicals.

Class I.

POSITIVE RADICALS.

Monads.

Methyl or $(C_nH_{2n+1})_2$ Series.
Vinyl, Allyl or $(C_nH_{2n-1})_2$ Series.
Phenyl or $(C_nH_{2n-7})_2$ Series.
Naphthyl or $(C_nH_{2n-13})_2$ Series.

Dyads.

Ethylene or C_nH_{2n} Series.
Acetylene or C_nH_{2n-2} Series.
Phenylene or C_nH_{2n-8} Series.

Triads.

Glyceryl or $(C_nH_{2n-1})'''_2$ Series.

Class I.

POSITIVE RADICALS.

MONADS.

METHYL or $(C_nH_{2n+1})_2$ *SERIES.*

These radicals are divided into three sections, viz., Normal,[*] Secondary, and Tertiary:—

	General formulæ.
1. Normal Radicals.......	$\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}(C_nH_{2n+1})H_2\end{array}\right.$
2. Secondary Radicals ..	$\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})_2H\\ \mathbf{C}(C_nH_{2n+1})_2H\end{array}\right.$
3. Tertiary Radicals	$\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})_3\\ \mathbf{C}(C_nH_{2n+1})_3\end{array}\right.$

In the first of the above formulæ n may $= 0$, but in the others it must be a positive integer.

Examples of the tertiary series of radicals may be seen in the tertiary alcohols and tertiary fatty acids. The radicals themselves have not yet been isolated.

It is evident that, besides the three series of radicals shown above, three other series, containing, in the same molecule, normal and secondary, normal and tertiary, and secondary and tertiary radicals, may exist; but up to the present time only one or two examples of such radicals are known.

By the action of zincic ethide on the chloride obtained from acetone by means of phosphoric chloride, a hydrocarbon is obtained, which may be regarded as a mixed normal and tertiary monad positive radical: ethyl etho-dimethomethyl or ethyl isoamyl:—

---

[*] Some writers on chemistry employ the term "primary" instead of "normal," reserving the latter term to designate those compounds in which the symbolic chain of carbon atoms has no branches.

$$\left\{\begin{matrix}CH_3\\ CMeCl_2\end{matrix}\right. + ZnEt_2 = ZnCl_2 + \left\{\begin{matrix}CMe_2Et\\ CMeH_2\end{matrix}\right. .$$

Chloride from acetone.	Zincic ethide.	Zincic chloride.	Ethyl etho-dimethomethyl.

1. *Normal Radicals.*

This series contains the radicals of the methyl series of alcohols.

These radicals also enter into the composition of the normal series of fatty acids.

The following list contains all the radicals of this section that have been hitherto obtained:—

		Boiling-points.
Methyl	$\left\{\begin{matrix}Me\\ Me'\end{matrix}\right.$ or $\left\{\begin{matrix}CH_3.\\ CH_3\end{matrix}\right.$	not known.
Ethyl	$\left\{\begin{matrix}Et\\ Et'\end{matrix}\right.$ or $\left\{\begin{matrix}CMeH_2\\ CMeH_2'\end{matrix}\right.$ or $\left\{\begin{matrix}CH_3\\ CH_2\\ CH_2\\ CH_3\end{matrix}\right.$	about −23°.
Propyl	$\left\{\begin{matrix}Pr\\ Pr'\end{matrix}\right.$ or $\left\{\begin{matrix}CEtH_2\\ CEtH_2\end{matrix}\right.$ or $\left\{\begin{matrix}CH_3\\ CH_2\\ CH_2\\ CH_2\\ CH_2\\ CH_3\end{matrix}\right.$	+68°.
Butyl	$\left\{\begin{matrix}Bu\\ Bu'\end{matrix}\right.$ or $\left\{\begin{matrix}CPrH_2\\ CPrH_2\end{matrix}\right.$	119°.
Amyl	$\left\{\begin{matrix}Ay\\ Ay'\end{matrix}\right.$ or $\left\{\begin{matrix}CBuH_2\\ CBuH_2\end{matrix}\right.$	159°.
Caproyl	$\left\{\begin{matrix}Cp\\ Cp'\end{matrix}\right.$ or $\left\{\begin{matrix}CAyH_2\\ CAyH_2\end{matrix}\right.$	202°.

Preparation.—1. By the action of zinc on the iodides of the normal radicals:—

$$2C(C_nH_{2n+1})H_2I + Zn = ZnI_2 + \left\{\begin{matrix}C(C_nH_{2n+1})H_2\\ C(C_nH_{2n+1})H_2\end{matrix}\right.$$

Part of the liberated radical is at the same time decomposed into the hydride of the radical and the corresponding dyad radical:—

$$\begin{cases} \mathbf{C}(C_nH_{2n+1})H_2 \\ \mathbf{C}(C_nH_{2n+1})H_2 \end{cases} = \begin{cases} \mathbf{C}(C_nH_{2n+1})H_2 \\ H \end{cases} + [\mathbf{C}(C_nH_{2n+1})H]''.$$

A remarkable special method for preparing ethyl consists in exposing mercury and ethylic iodide to the influence of sunlight:—

$$\underset{\substack{\text{Ethylic}\\\text{iodide.}}}{2EtI} + Hg = \underset{\substack{\text{Mercuric}\\\text{iodide.}}}{\mathbf{Hg}I_2} + \underset{\text{Ethyl.}}{Et_2}.$$

2. By the electrolysis of the salts of the normal fatty acids. In this process the electropositive metal goes to the negative electrode, and the rest of the molecule splits up into two groups; thus with a potassium salt:—

$$\underset{\text{Fatty acid.}}{2\begin{cases} \mathbf{C}(C_nH_{2n+1})H_2 \\ \mathbf{CO}Ko \end{cases}} = \underset{\text{Radical.}}{\begin{cases} \mathbf{C}(C_nH_{2n+1})H_2 \\ \mathbf{C}(C_nH_{2n+1})H_2 \end{cases}}$$

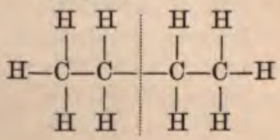
$$+ \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{2\mathbf{CO}_2} + \underset{\text{Potassium.}}{K_2}.$$

3. By acting with zinc upon the iodides of two radicals simultaneously, the so-called double or mixed radicals are produced:—

$$\underset{\substack{\text{Methylic}\\\text{iodide.}}}{MeI} + \underset{\substack{\text{Ethylic}\\\text{iodide.}}}{EtI} + Zn = \underset{\substack{\text{Zincic}\\\text{iodide.}}}{\mathbf{Zn}I_2} + \underset{\substack{\text{Methyl}\\\text{ethyl.}}}{\begin{cases} Me \\ Et \end{cases}}.$$

ETHYL.

$$\begin{cases} \mathbf{C}MeH_2 \\ \mathbf{C}MeH_2 \end{cases}$$



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\,|\,-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

Molecular weight = 58. *Molecular volume* $\square\!\square$. 1 *litre of ethyl gas weighs* 29 *criths. Boils at about* − 23° C.

Preparation.—By digesting together in a close vessel at

120° ethylic iodide and zinc, the reaction being similar to that between hydriodic acid and zinc:—

$$\mathrm{Zn} + \underset{\text{Hydriodic acid.}}{2\mathrm{HI}} = \underset{\text{Zincic iodide.}}{\mathrm{ZnI_2}} + \underset{\text{Hydrogen.}}{\left\{\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right.}$$

$$\mathrm{Zn} + \underset{\text{Ethylic iodide.}}{2\mathrm{EtI}} = \underset{\text{Zincic iodide.}}{\mathrm{ZnI_2}} + \underset{\text{Ethyl.}}{\left\{\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\right.}$$

2. *Secondary Radicals.*

Two secondary monad positive radicals are known:—

Isopropyl ...... $\left\{\begin{matrix}\mathrm{CMe_2H}\\ \mathrm{CMe_2H}\end{matrix}\right.$ .... boils at 58°

Amyl-isopropyl .. $\left\{\begin{matrix}\mathrm{CMe_2H}\\ \mathrm{CBuH_2}\end{matrix}\right.$ .... „ „ 110°

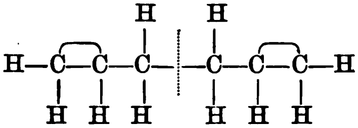
VINYL OR ALLYL SERIES.

General formula.. $\left\{\begin{matrix}\mathrm{C(C_nH_{2n-1})H_2}\\ \mathrm{C(C_nH_{2n-1})H_2}\end{matrix}\right.$.

The first member of this series, vinyl, has not yet been isolated.

ALLYL.

$$\left\{\begin{matrix}\mathrm{C_3H_5}\\ \mathrm{C_3H_5}\end{matrix}\right. \text{ or } \left\{\begin{matrix}\mathrm{C(CMe''H)H_2}\\ \mathrm{C(CMe''H)H_2}\end{matrix}\right.$$



Molecular weight = 82. *Molecular volume* ☐☐. 1 *litre of allyl vapour weighs* 41 *criths. Sp. gr.* 0·684. *Boils at* 59°.

Preparation.—By digesting allylic iodide with sodium, and then distilling:—

$$\mathrm{Na_2} + \underset{\textit{Allylic iodide.}}{2\mathrm{C(CMe''H)H_2I}} = \underset{\text{Allyl.}}{\left\{\begin{matrix}\mathrm{C(CMe''H)H_2}\\ \mathrm{C(CMe''H)H_2}\end{matrix}\right.} + \underset{\text{Sodic iodide.}}{2\mathrm{NaI}}.$$

Character.—Bromine and iodine unite directly with allyl, producing allylic tetrabromide and tetriodide. In these compounds the molecule of allyl plays the part of a tetrad radical.

In allylic tetrabromide, four latent carbon bonds in the molecule of allyl have become active, and have united with four atoms of bromine:—

$$\underset{\text{Allyl.}}{\left\{\begin{array}{l}\mathbf{C}(\mathrm{CMe''H})\mathrm{H}_2\\ \mathbf{C}(\mathrm{CMe''H})\mathrm{H}_2\end{array}\right.} + \mathrm{Br}_4 = \underset{\text{Allylic tetrabromide.}}{\left\{\begin{array}{l}\mathbf{C}[\mathrm{C}(\mathrm{CH_2Br})\mathrm{BrH}]\mathrm{H}_2\\ \mathbf{C}[\mathrm{C}(\mathrm{CH_2Br})\mathrm{BrH}]\mathrm{H}_2\end{array}\right.}\cdot$$

An analogous case is met with in ferric chloride, where two tetrad atoms, united by one bond of each, become together hexadic:—

$$\left\{\begin{array}{l}\mathbf{Fe}\mathrm{Cl}_3\\ \mathbf{Fe}\mathrm{Cl}_3\end{array}\right.\cdot$$

Allylic monobromide can only be obtained by the action of phosphorous tribromide on allylic alcohol:—

$$\underset{\text{Allylic alcohol.}}{3\mathbf{C}(\mathrm{CMe''H})\mathrm{H_2Ho}} + \underset{\substack{\text{Phosphorous}\\ \text{tribromide.}}}{\mathbf{P}\mathrm{Br}_3} = \underset{\text{Allylic monobromide.}}{3\mathbf{C}(\mathrm{CMe''H})\mathrm{H_2Br}}$$

$$+ \underset{\text{Phosphorous acid.}}{\mathbf{P}\mathrm{OHHo}_2.}$$

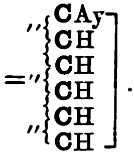
PHENYL SERIES.

General formula.. $\left\{\begin{array}{l}\mathrm{C}_n\mathrm{H}_{2n-7}\\ \mathrm{C}_n\mathrm{H}_{2n-7}\end{array}\right.\cdot$

The following have been isolated:—

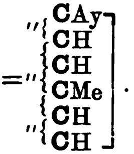
Phenyl	$\left\{\begin{array}{l}\mathrm{C_6H_5}\\ \mathrm{C_6H_5}\end{array}\right.\cdot$
Tolyl	$\left\{\begin{array}{l}\mathrm{C_6H_4Me}\\ \mathrm{C_6H_4Me}\end{array}\right.\cdot$
Benzyl..................	$\left\{\begin{array}{l}\mathrm{CH_2(C_6H_5)}\\ \mathrm{CH_2(C_6H_5)}\end{array}\right.\cdot$

Amyl benzene or amyl phenyl.. $C_6H_5(C_5H_{11})$ =



$$=\left[\begin{array}{l} ''\{CAy \\ \;\;\{CH \\ \;\;\{CH \\ ''\{CH \\ \;\;\{CH \\ ''\{CH \end{array}\right].$$

Amyl toluene or amyl tolyl .. $C_6H_4(CH_3)(C_5H_{11})$ =

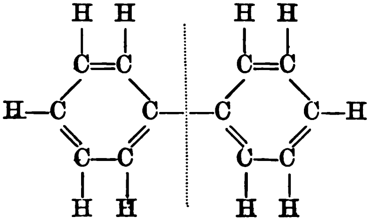


$$=\left[\begin{array}{l} ''\{CAy \\ \;\;\{CH \\ \;\;\{CH \\ ''\{CMe \\ \;\;\{CH \\ ''\{CH \end{array}\right].$$

Amyl xylene .... $C_6H_3(CH_3)_2(C_5H_{11})$.

PHENYL..

$$\begin{cases} C_6H_5 \\ C_6H_5 \end{cases}.$$



Molecular weight = 154. *Molecular volume* ☐☐. 1 *litre of phenyl vapour weighs* 77 *criths. Fuses at* 70·5°. *Boils at* 254°.

Preparation.—1. By the action of sodium on phenylic bromide:—

$$\underset{\text{Phenylic bromide.}}{2C_6H_5Br} + Na_2 = \underset{\text{Phenyl.}}{\begin{cases} C_6H_5 \\ C_6H_5 \end{cases}} + \underset{\text{Sodic bromide.}}{2NaBr}.$$

2. By passing the vapour of benzene through a red-hot tube:—

$$\underset{\text{Benzene}}{2C_6H_6} = \underset{\text{Phenyl}}{\begin{cases} C_6H_5 \\ C_6H_5 \end{cases}} + H_2.$$

Reaction.—By treatment with bromine, phenyl produces bromphenyl and hydrobromic acid:—

$$\underset{\text{Phenyl.}}{\left\{\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right.} + Br_4 = \underset{\text{Bromphenyl.}}{\left\{\begin{matrix}C_6H_4Br\\C_6H_4Br\end{matrix}\right.} + \underset{\text{Hydrobromic acid.}}{2HBr.}$$

NAPHTHYL SERIES.

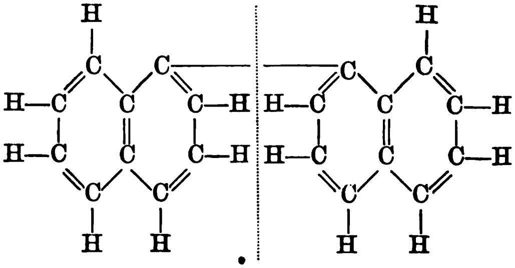
General formula.. $\left\{\begin{matrix}C_nH_{2n-13}\\C_nH_{2n-13}\end{matrix}\right.$.

The radical naphthyl has alone been isolated, but it is known in three isomeric modifications, distinguished as *αα*-, *ββ*-, and *αβ*-naphthyl (see p. 71).

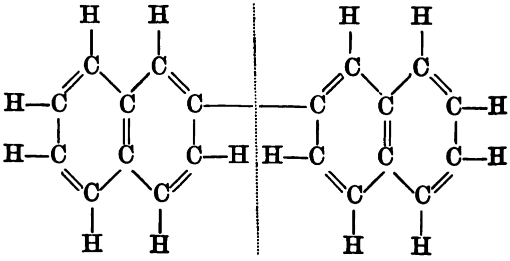
NAPHTHYL.

$$\left\{\begin{matrix}C_{10}H_7\\C_{10}H_7\end{matrix}\right. .$$

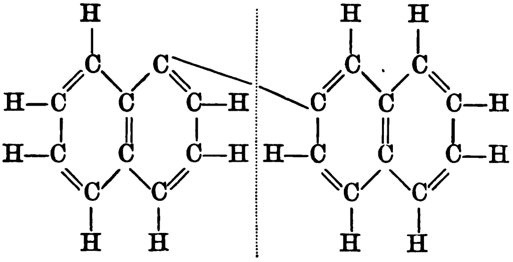
αα-Naphthyl.



ββ-Naphthyl.



αβ-Naphthyl.



Molecular weight = 254. *Molecular volume* ☐☐. 1 *litre of naphthyl vapour weighs* 127 *criths. αα fuses at* 154°; *ββ at* 187°; *αβ at* 76°. *All three boil about* 440°.

Preparation.—1. By the action of sodium on naphthylic bromide:—

$$\underset{\text{Naphthylic bromide.}}{2C_{10}H_7Br} + Na_2 = \underset{\text{Naphthyl.}}{\begin{cases} C_{10}H_7 \\ C_{10}H_7 \end{cases}} + \underset{\text{Sodic bromide.}}{2NaBr.}$$

2. By treating naphthalene with oxidising agents:—

$$\underset{\text{Naphthalene.}}{2C_{10}H_8} + O = \underset{\text{Naphthyl.}}{\begin{cases} C_{10}H_7 \\ C_{10}H_7 \end{cases}} + \underset{\text{Water.}}{OH_2.}$$

CHAPTER III.

POSITIVE RADICALS.

DYADS.

ETHYLENE or C_nH_{2n} *SERIES.*

Preparation.—These compounds are produced as follows:—

1. In many cases of destructive distillation, where, however, the reaction cannot be traced.

2. By the abstraction of the elements of water from the normal monohydric alcohols of the methyl series, as for instance:—

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}CH_3\\CH_2Ho\end{matrix}\right.} = \underset{\text{Ethylene.}}{{}''\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.} + \underset{\text{Water.}}{OH_2.}$$

3. By passing the vapours of the haloid compounds of the normal monad radicals of the C_nH_{2n+1} series over heated lime, thus:—

$$\underset{\text{Ethylic chloride.}}{\left\{\begin{matrix}CH_3\\CH_2Cl\end{matrix}\right.} = \underset{\text{Ethylene.}}{{}''\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl.}$$

4. By the transformation of the monad radicals at the moment of liberation from their compounds, when they split into dyad radicals and the hydrides of monad radicals:—

$$\underset{\text{Ethyl.}}{\left\{\begin{matrix}C(CH_3)H_2\\C(CH_3)H_2\end{matrix}\right.} = \underset{\text{Ethylene.}}{{}''\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.} + \underset{\text{Ethylic hydride.}}{\left\{\begin{matrix}CH_3\\CH_3.\end{matrix}\right.}$$

5. By the action of the iodide of a monad radical on the sodium compound of a monad radical:—

$$\underset{\text{Ethylic iodide.}}{\left\{\begin{matrix}CH_3\\CH_2I\end{matrix}\right.} + \underset{\text{Sodic ethide.}}{\left\{\begin{matrix}CH_3\\CH_2Na\end{matrix}\right.} = \underset{\text{Sodic iodide.}}{NaI} + \underset{\text{Ethylene.}}{{}''\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.} + \underset{\text{Ethylic hydride.}}{\left\{\begin{matrix}CH_3\\CH_3.\end{matrix}\right.}$$

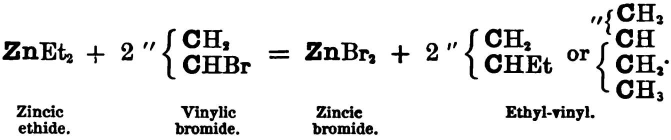
6. Methylic iodide and allylic iodide dissolved in ether and digested with sodium in sealed vessels produce methyl-allyl, an isomer of butylene:—

$$\underset{\text{Methylic iodide.}}{CH_3I} + \underset{\text{Allylic iodide.}}{{}''\left\{\begin{matrix}CH_2\\CH\\CH_2I\end{matrix}\right.} + Na_2 = 2NaI + \underset{\text{Methyl-allyl.}}{{}''\left\{\begin{matrix}CH_2\\CH.\\CH_2\\CH_3\end{matrix}\right.}$$

7. By the action of zincic ethide on allylic iodide, ethyl-allyl, isomeric with amylene, is obtained:—

$$\underset{\text{Zincic ethide.}}{ZnEt_2} + 2\,\underset{\text{Allylic iodide.}}{{}''\left\{\begin{matrix}CH_2\\CH\\CH_2I\end{matrix}\right.} = \underset{\text{Zincic iodide.}}{ZnI_2} + 2\,{}''\left\{\begin{matrix}CH_2\\CH\\CH_2Et\end{matrix}\right. \text{ or } \underset{\text{Ethyl-allyl.}}{{}''\left\{\begin{matrix}CH_2\\CH\\CH_2.\\CH_2\\CH_2\end{matrix}\right.}$$

8. By treatment of vinylic bromide (brominated ethylene) with zincic ethide, ethyl-vinyl, isomeric with butylene, is produced:—



$$\underset{\text{Zincic ethide.}}{ZnEt_2} + 2''\underset{\text{Vinylic bromide.}}{\left\{\begin{matrix}CH_2\\CHBr\end{matrix}\right.} = \underset{\text{Zincic bromide.}}{ZnBr_2} + 2''\left\{\begin{matrix}CH_2\\CHEt\end{matrix}\right. \text{ or } ''\left\{\begin{matrix}CH_2\\CH\\CH_2\\CH_3\end{matrix}\right. \cdot \quad \text{Ethyl-vinyl.}$$

Methyl-allyl is stated to differ from ethyl-vinyl, but in this case a migration of atoms must occur during one of these reactions, and the corresponding symbolic formula here given is incorrect.

Character.—The lower members of this series of dyad radicals are gaseous, the higher solid, and the intermediate ones liquid.

The following list includes the known dyad radicals of this series, together with their fusing- and boiling-points:—

		Fusing-point.	Boiling-point.
Ethylene	C_2H_4	—	—
Propylene	C_3H_6	—	−17·8°
Pseudobutylene	C_4H_8	—	− 7·0
Isobutylene	C_4H_8	—	− 5·0
Butylene	C_4H_8	—	+ 3·0
Amylene	C_5H_{10}	—	35·0
Hexylene	C_6H_{12}	—	39·0
Heptylene or Œnanthylene	C_7H_{14}	—	55·0
Octylene or Caprylene	C_8H_{16}	—	95·0
Nonylene	C_9H_{18}	—	125·0
Paramylene	$C_{10}H_{20}$	—	—
Cetene	$C_{16}H_{32}$	—	—
Cerotene	$C_{27}H_{54}$	57°	275·0
Melene	$C_{30}H_{60}$	62	375·0

Reactions.—1. The dyad radicals of this series all unite directly with chlorine, bromine, and iodine, producing compounds which, in the case of ethylene, are represented by

$$\begin{array}{ccc}\left\{\begin{array}{l}CH_2Cl\\ CH_2Cl\end{array}\right. & \left\{\begin{array}{l}CH_2Br\\ CH_2Br\end{array}\right. & \left\{\begin{array}{l}CH_2I\\ CH_2I\cdot\end{array}\right.\\ \text{Ethylenic dichloride.} & \text{Ethylenic dibromide.} & \text{Ethylenic diiodide.}\end{array}$$

These compounds, when treated with alcoholic solution of potassic hydrate, lose one molecule of a hydracid, thus:—

$$\begin{array}{ccccccccc}\left\{\begin{array}{l}CH_2Cl\\ CH_2Cl\end{array}\right. & + & KHo & = & KCl & + & {}''\left\{\begin{array}{l}CH_2\\ CHCl\end{array}\right. & + & OH_2.\\ \text{Ethylenic dichloride.} & & \text{Potassic hydrate.} & & \text{Potassic chloride.} & & \text{Vinylic chloride, or chlorinated ethylene.} & & \text{Water.}\end{array}$$

The monochlorinated radical thus obtained again unites with two atoms of chlorine, producing chlorinated ethylidenic dichloride,

$$\left\{\begin{array}{l}CH_2Cl\\ CHClCl,\end{array}\right.$$

which, by further treatment with alcoholic potash, yields unsymmetrical dichlorinated ethylene; and so, by alternate treatments with chlorine and potassic hydrate, ethylene becomes transformed into tetrachlorinated ethylene. The following formulæ show the first, intermediate, and final compounds:—

$$''\left\{\begin{array}{l}CH_2\\ CH_2\end{array}\right. \quad \left\{\begin{array}{l}CH_2Cl\\ CH_2Cl\end{array}\right. \quad ''\left\{\begin{array}{l}CH_2\\ CHCl\end{array}\right. \quad \left\{\begin{array}{l}CH_2Cl\\ CHClCl\end{array}\right. \quad ''\left\{\begin{array}{l}CH_2\\ CCl_2\end{array}\right.$$

$$\left\{\begin{array}{l}CH_2Cl\\ CCl_2Cl\end{array}\right. \quad ''\left\{\begin{array}{l}CHCl\\ CCl_2\end{array}\right. \quad \left\{\begin{array}{l}CHClCl\\ CCl_2Cl\end{array}\right. \quad ''\left\{\begin{array}{l}CCl_2\\ CCl_2\cdot\end{array}\right.$$

Tetrachlorinated ethylene absorbs two additional atoms of chlorine, producing the solid dicarbonic hexachloride:—

$$\left\{\begin{array}{l}CCl_3\\ CCl_3\cdot\end{array}\right.$$

Dicarbonic hexachloride.

2. The dyad radicals of the ethylene series can be transformed into the monad radicals from which they are derived. If ethylene be digested with hydriodic acid for 50 hours at 100° C., it is transformed into ethylic iodide:—

$$\underset{\text{Ethylene.}}{{}''\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.} + \underset{\text{Hydriodic acid.}}{HI} = \underset{\text{Ethylic iodide.}}{\left\{\begin{matrix}CH_3\\CH_2I\end{matrix}\right.}$$

From this ethyl may be prepared, as shown at p. 12.

Isomerism of ethylene and ethylidene compounds.—The chlorides of the dyad radicals are isomeric:—

1. With the chlorides of the monochlorinated normal monad radicals.

2. With the chlorides derived from the aldehydes, which, however, are identical with the chlorides of the monochlorinated normal monad radicals:—

$$\underset{\text{Ethylenic dichloride.}}{\left\{\begin{matrix}CH_2Cl\\CH_2Cl\end{matrix}\right.} \qquad \underset{\text{Ethylidenic dichloride (obtained from aldehyde.)}}{\left\{\begin{matrix}CH_3\\CHCl_2\end{matrix}\right.} \qquad \underset{\text{Monochlorinated ethylic chloride.}}{\left\{\begin{matrix}CH_3\\CHCl_2\end{matrix}\right.}$$

These substances, when treated with alcoholic potash, all yield the same vinylic chloride:—

$$\underset{\text{Ethylenic dichloride.}}{\left\{\begin{matrix}CH_2Cl\\CH_2Cl\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Vinylic chloride.}}{{}''\left\{\begin{matrix}CH_2\\CHCl\end{matrix}\right.} + \underset{\text{Water.}}{OH_2} + \underset{\text{Potassic chloride.}}{KCl.}$$

$$\underset{\text{Monochlorinated ethylic chloride, or Ethylidenic dichloride.}}{\left\{\begin{matrix}CH_3\\CHCl_2\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Vinylic chloride.}}{{}''\left\{\begin{matrix}CH_2\\CHCl\end{matrix}\right.} + \underset{\text{Water.}}{OH_2} + \underset{\text{Potassic chloride.}}{KCl.}$$

But certain compounds of ethylene yield hydracrylic acid, whilst the corresponding compounds of ethylidene give lactic acid. The boiling-points of their chlorides also differ, ethylenic dichloride boiling at 85°, whilst ethylidenic dichloride boils at 57°·5; on the other hand, ethylenic oxide boils at 13°·5, whilst ethylidenic oxide (aldehyde) boils at 21°.

The oxides of the dyad radicals are isomeric:—

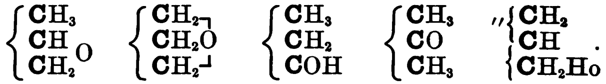
1. With the oxides of isomeric dyad radicals.

2. With the corresponding aldehydes.

3. With the ketones containing the same number of atoms of carbon.

4. With the alcohols of the allylic or $C_nH_{2n-1}Ho$ series.

The nature of this isomerism is seen from the following formulæ:—

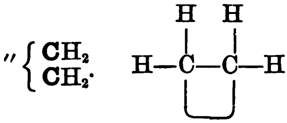


$$\left\{\begin{matrix}CH_3\\CH\\CH_2\end{matrix}\right.O \quad \left\{\begin{matrix}CH_2\\CH_2O\\CH_2\end{matrix}\right. \quad \left\{\begin{matrix}CH_3\\CH_2\\COH\end{matrix}\right. \quad \left\{\begin{matrix}CH_3\\CO\\CH_3\end{matrix}\right. \quad {}''\left\{\begin{matrix}CH_2\\CH\\CH_2Ho\end{matrix}\right. .$$

Propylenic oxide. Trimethylenic oxide. Propionic aldehyde. Acetone. Allylic alcohol.

All of these compounds are known.

ETHYLENE.

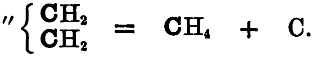


$${}''\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right. .$$

Molecular weight = 28. *Molecular volume* $\boxed{}\boxed{}$. 1 *litre weighs* 14 *criths.*

Preparation.—See general methods (pp. 17 and 18).

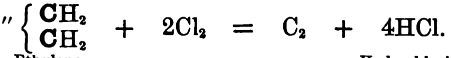
Reactions.—1. Decomposed into carbon and marsh-gas by passing through a red-hot tube:—



$${}''\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right. = CH_4 + C.$$

Ethylene. Marsh-gas.

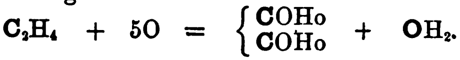
2. Burns in chlorine with deposition of carbon:—



$${}''\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right. + 2Cl_2 = C_2 + 4HCl.$$

Ethylene. Hydrochloric acid.

3. Ethylene when agitated with solution of potassic permanganate is oxidized, oxalic acid, formic acid, and carbonic anhydride being formed:—



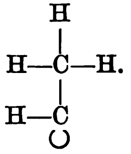
$$C_2H_4 + 5O = \left\{\begin{matrix}COHo\\COHo\end{matrix}\right. + OH_2.$$

Ethylene. Oxalic acid. Water.

$$\underset{\text{Ethylene.}}{C_2H_4} + 5O = \underset{\text{Formic acid.}}{\left\{\begin{matrix} H \\ COHo \end{matrix}\right.} + \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Water.}}{OH_2.}$$

Ethylidene, the isomer of ethylene, has not yet been isolated. The constitutional formula of ethylidene is

$$\left\{\begin{matrix} CH_3 \\ ''CH \end{matrix}\right. \cdot$$



$$\begin{array}{c} H \\ | \\ H—C—H. \\ | \\ H—C \\ \circ \end{array}$$

ACETYLENE or C_nH_{2n-2} SERIES.

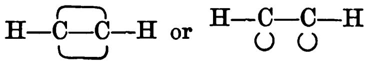
Acetylene is the radical belonging to this series which is best known. The series comprises the following members:—

Acetylene	C_2H_2.
Allylene	C_3H_4.
Crotonylene	C_4H_6.
Valerylene	C_5H_8.

These radicals stand in the same relation to the alcohols of the allylic series as ethylene bears to ethylic alcohol. They are also capable of assuming tetrad functions.

ACETYLENE.

$'''C'_2H_2$ or $\left\{\begin{matrix} ''CH \\ ''CH \end{matrix}\right. \cdot$



Molecular weight = 26. *Molecular volume* $\square\!\square$. 1 *litre weighs* 13 *criths. Liquefies at* 0° *under a pressure of* 21·5 *atmospheres. Critical point* 37°. *Sp. gr. of liquid at* 0° 0·451.

Preparation.—1. By synthesis from its elements. When an electric arc from a moderately powerful voltaic battery passes between carbon poles in an atmosphere of hydrogen, acetylene is produced.

2. By the action of water on potassic or calcic carbide :—

$$\underset{\text{Potassic carbide.}}{\mathbf{C}_2K_2} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Acetylene.}}{\mathbf{C}_2H_2} + \underset{\text{Potassic hydrate.}}{2KHo.}$$

$$\underset{\text{Calcic carbide.}}{\mathbf{C}_2Ca''} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Acetylene.}}{\mathbf{C}_2H_2} + \underset{\text{Calcic hydrate.}}{\mathbf{Ca}Ho_2.}$$

3. By the action of heat upon olefiant gas or the vapour of alcohol, ether, or wood-spirit, or by passing electric sparks through marsh-gas :—

$$\underset{\text{Marsh-gas.}}{2\mathbf{C}H_4} = \underset{\text{Acetylene.}}{\mathbf{C}_2H_2} + 3H_2.$$

4. By heating the vapour of methylic chloride to low redness :—

$$\underset{\text{Methylic chloride.}}{2\mathbf{C}H_3Cl} = \underset{\text{Acetylene.}}{\mathbf{C}_2H_2} + \underset{\text{Hydrochloric acid.}}{2HCl} + H_2.$$

5. By passing the vapour of chloroform over ignited copper :—

$$\underset{\text{Chloroform.}}{2\mathbf{C}HCl_3} + Cu_6 = \underset{\text{Acetylene.}}{\mathbf{C}_2H_2} + \underset{\text{Cuprous chloride.}}{3'\mathbf{Cu}'_2Cl_2.}$$

6. From vinylic bromide, one of the derivatives of ethylene, acetylene may be obtained by the action of alcoholic potash :—

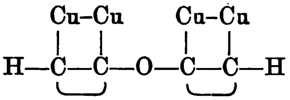
$$\underset{\text{Vinylic bromide.}}{\mathbf{C}_2H_3Br} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Acetylene.}}{\mathbf{C}_2H_2} + \underset{\text{Potassic bromide.}}{KBr} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

7. By the incomplete combustion of bodies containing carbon and hydrogen :—

$$\underset{\text{Marsh-gas.}}{4\mathbf{C}H_4} + 3O_2 = \underset{\text{Acetylene.}}{2\mathbf{C}_2H_2} + \underset{\text{Water.}}{6\mathbf{O}H_2:}$$

$$\underset{\text{Olefiant gas.}}{2\mathbf{C}_2H_4} + O_2 = \underset{\text{Acetylene.}}{2\mathbf{C}_2H_2} + \underset{\text{Water.}}{2\mathbf{O}H_2.}$$

The crude acetylene, obtained by any of these processes, is best purified by passing it through an ammoniacal solution of cuprous chloride, with which it forms a red precipitate, containing $\left\{\begin{matrix}\mathbf{C}_2'Cu'_2H\\ O\\ \mathbf{C}_2'Cu'_2H\end{matrix}\right.$.



$$\begin{matrix} & & Cu & - & Cu & & & & Cu & - & Cu & & \\ & & | & & | & & & & | & & | & & \\ H & — & C & — & C & — & O & — & C & — & C & — & H\end{matrix}$$

$$2'\mathbf{Cu}'_2Cl_2 \;+\; 2\mathbf{C}_2H_2 \;+\; \mathbf{O}H_2 \;=\; \left\{\begin{matrix}\mathbf{C}_2'Cu'_2H\\ O\\ \mathbf{C}_2'Cu'_2H\end{matrix}\right. \;+\; 4HCl.$$

Cuprous chloride. — Acetylene. — Cuprosovinylic ether. (Acetylide of copper.) — Hydrochloric acid.

If ethylene has been present in the crude acetylene, the liquid containing the red precipitate is next heated to boiling, in order to decompose a compound which ethylene forms with copper. The cuprosovinylic ether is then collected upon a filter and washed. On heating cuprosovinylic ether with hydrochloric acid, pure acetylene is evolved :—

$$\left\{\begin{matrix}\mathbf{C}_2'Cu'_2H\\ O\\ \mathbf{C}_2'Cu'_2H\end{matrix}\right. \;+\; 4HCl \;=\; 2\mathbf{C}_2H_2 \;+\; 2'\mathbf{Cu}'_2Cl_2 \;+\; \mathbf{O}H_2.$$

Cuprosovinylic ether. (Acetylide of copper.) — Hydrochloric acid. — Acetylene. — Cuprous chloride. — Water.

Reactions.—1. When cuprosovinylic ether is heated with zinc and dilute ammonia, the nascent hydrogen, evolved by the action of the zinc upon the ammonia, unites with acetylene, producing ethylene :—

$$\left\{\begin{matrix}\mathbf{C}_2'Cu'_2H\\ O\\ \mathbf{C}_2'Cu'_2H\end{matrix}\right. \;+\; 2H_2 \;=\; 2\mathbf{C}_2H_2 \;+\; 4Cu \;+\; \mathbf{O}H_2;$$

Cuprosovinylic ether. — Acetylene. — Water.

$$\mathbf{C}_2H_2 \;+\; H_2 \;=\; \mathbf{C}_2H_4.$$

Acetylene. — Ethylene.

2. Acetylene unites with bromine, forming acetylenic dibromide :—

$$'''\mathbf{C}'_2H_2 \;+\; Br_2 \;=\; ''\mathbf{C}''_2H_2Br_2.$$

Acetylene. — Acetylenic dibromide.

This compound combines in its turn with another molecule of bromine, forming acetylenic tetrabromide:—

$$\underset{\text{Acetylenic dibromide.}}{''C''_2H_2Br_2} + Br_2 = \underset{\text{Acetylenic tetrabromide.}}{C_2H_2Br_4.}$$

3. By agitating acetylene with solution of potassic permanganate, oxalic acid is formed:—

$$\underset{\text{Acetylene.}}{'''\left\{\begin{matrix}CH\\CH\end{matrix}\right.} + 2O_2 = \underset{\text{Oxalic acid.}}{\left\{\begin{matrix}COHo\\COHo\end{matrix}\right.}\cdot$$

Carbonic anhydride and formic acid are simultaneously produced:—

$$'''\left\{\begin{matrix}CH\\CH\end{matrix}\right. + 2O_2 = \left\{\begin{matrix}H\\COHo\end{matrix}\right. + CO_2.$$

BROMACETYLENE.

C_2HBr.

By boiling together dibromethylenic dibromide with alcoholic potash, a spontaneously inflammable gas is evolved, which is bromacetylene:—

$$\underset{\text{Dibromethylenic dibromide.}}{\left\{\begin{matrix}CHBrBr\\CHBrBr\end{matrix}\right.} = \underset{\text{Hydrobromic acid.}}{HBr} + Br_2 + \underset{\text{Bromacetylene.}}{C_2HBr.}$$

PHENYLENE or C_nH_{2n-8} *SERIES.*

The dyad radicals of this series are very little known. The following has been isolated:—

$$\text{Benzylene or Stilbene, } ''\left\{\begin{matrix}C(C_6H_5)H\\C(C_6H_5)H\end{matrix}\right.\cdot$$

POSITIVE RADICALS.

TRIADS.

These radicals are unknown in the separate state, unless they are identical with the dyad radicals of the acetylene series :—

$$\underset{\text{Acetylene.}}{C_2H_2} = \underset{\text{Formyl.}}{\left\{\begin{matrix}(CH)'''\\(CH)'''\end{matrix}\right.}$$

They are, however, well known in a numerous class of compounds belonging to families which will be studied hereafter.

CHAPTER IV.

ORGANIC RADICALS.

Class II.

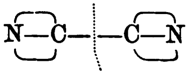
NEGATIVE RADICALS.

Every positive radical may be looked upon as the source of a negative radical, which is generated by displacing a portion of the hydrogen of the former by oxygen. Thus :—

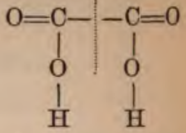
Ethyl	$\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$	yields	acetyl	$\left\{\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right.$
Allyl	$\left\{\begin{matrix}C_3H_5\\C_3H_5\end{matrix}\right.$	,,	acryl	$\left\{\begin{matrix}C_3H_3O\\C_3H_3O\end{matrix}\right.$
Ethylene	$(C_2H_4)''$	,,	glycolyl	$(C_2H_2O)''$.
Propylene	$(C_3H_6)''$	,,	lactyl	$(C_3H_4O)''$.
,,		,,	malonyl	$(C_3H_2O_2)''$.

The constitution of the so-called compounds of these negative radicals may, however, be more simply explained from another point of view; and, in fact it will rarely be necessary for us to recognize the existence of more than two negative radicals, in order to understand the whole range of negative organic compounds. These are:—

Cyanogen .... $\left\{\begin{matrix}CN'''\\CN'''\end{matrix}\right.$



Oxatyl, the molecule of which is dry oxalic acid. $\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}OHo\end{array}\right.$.



These two radicals are the acidifying principles of nearly all organic acids; they are, therefore, highly important compounds. The semimolecule of each consists of an atom of carbon, one bond of which is free to combine with other elements or groups of elements, the other three bonds being saturated, in cyanogen by triad nitrogen, and in oxatyl by one atom of oxygen and one semimolecule of hydroxyl. In the molecules of both, the two free bonds of the carbon saturate each other.

These radicals are closely related to each other. Thus, if cyanogen be dissolved in water, it is soon transformed into ammonic oxalate:—

$$\underset{\text{Cyanogen.}}{\left\{\begin{array}{l}\mathbf{C}N'''\\ \mathbf{C}N'''\end{array}\right.} + \underset{\text{Water.}}{4\mathbf{O}H_2} = \underset{\text{Ammonic oxalate.}}{\left\{\begin{array}{l}\mathbf{C}O(N^{v}H_4O)\\ \mathbf{C}O(N^{v}H_4O)\end{array}\right.}.$$

In the presence of potassic hydrate, cyanogen evolves ammonia and produces potassic oxalate:—

$$\underset{\text{Cyanogen.}}{\left\{\begin{array}{l}\mathbf{C}N'''\\ \mathbf{C}N'''\end{array}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Potassic oxalate.}}{\left\{\begin{array}{l}\mathbf{C}OKo\\ \mathbf{C}OKo\end{array}\right.} + \underset{\text{Ammonia.}}{2\mathbf{N}H_3}.$$

From these salts oxalic acid, or the molecule of oxatyl, may be readily obtained by the action of sulphuric acid.

In the converse manner, oxatyl may be converted into cyanogen, by transforming it into ammonic oxalate and submitting this salt to the action of heat:—

$$\underset{\text{Ammonic oxalate.}}{\left\{\begin{array}{l}\mathbf{C}O(N^{v}H_4O)\\ \mathbf{C}O(N^{v}H_4O)\end{array}\right.} = \underset{\text{Water.}}{4\mathbf{O}H_2} + \underset{\text{Cyanogen.}}{\left\{\begin{array}{l}\mathbf{C}N'''\\ \mathbf{C}N'''\end{array}\right.}.$$

CYANOGEN.

$$\left\{\begin{matrix}CN'''\\ CN'''\end{matrix}\right. \text{ or } Cy_2.$$

Molecular weight = 52. *Molecular volume* □□. 1 *litre weighs* 26 *criths*. *Fuses at* −34°. *Boils at* −20°·7.

Occurrence.—Amongst the gases of blast furnaces,—a proof of its withstanding an extremely high temperature.

Preparation.—By the action of heat on mercuric cyanide:—

$$\underset{\substack{\text{Mercuric}\\ \text{cyanide.}}}{HgCy_2} = Hg + \underset{\text{Cyanogen.}}{Cy_2}.$$

This equation only partially expresses the reaction, as a brown non-volatile compound (paracyanogen), Cy$_n$, is simultaneously produced.

Reaction.—1. Cyanogen unites directly with potassium:—

$$\underset{\text{Cyanogen.}}{Cy_2} + K_2 = \underset{\substack{\text{Potassic}\\ \text{cyanide.}}}{2KCy}.$$

2. Cyanogen acts upon zinc ethyl, yielding zincic cyanide and abnormal ethylic cyanide (propionitrile):—

$$\underset{\text{Cyanogen.}}{2\left\{\begin{matrix}CN\\ CN\end{matrix}\right.} + \underset{\text{Zinc ethyl.}}{ZnEt_2} = \underset{\text{Propionitrile.}}{2Et(CN)} + \underset{\text{Zincic cyanide.}}{Zn(CN)_2}.$$

HYDROCYANIC ACID.

$$\left\{\begin{matrix}H\\ NC\end{matrix}\right. \text{ or } HCy.$$

Molecular weight = 27. *Molecular volume* □□. 1 *litre of hydrocyanic acid vapour weighs* 13·5 *criths*. *Sp. gr. of liquid* 0·7058. *Fuses at* −15°. *Boils at* 26°·5.

Preparation.—1. In the anhydrous condition, by passing hydrosulphuric acid over mercuric cyanide:—

$$\underset{\substack{\text{Mercuric}\\ \text{cyanide.}}}{HgCy_2} + \underset{\substack{\text{Sulphuretted}\\ \text{hydrogen.}}}{SH_2} = \underset{\substack{\text{Mercuric}\\ \text{sulphide.}}}{HgS''} + \underset{\substack{\text{Hydrocyanic}\\ \text{acid.}}}{2HCy}.$$

2. By distilling potassic cyanide, or ferrocyanide, with dilute sulphuric acid:—

$$\underset{\text{Potassic cyanide.}}{2KCy} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Hydrocyanic acid.}}{2HCy} + \underset{\text{Potassic sulphate.}}{SO_2Ko_2}.$$

3. By passing nitrogen over an ignited mixture of potassic carbonate and carbon:—

$$\underset{\text{Potassic carbonate.}}{COKo_2} + C_4 + N_2 = \underset{\text{Potassic cyanide.}}{2KCy} + \underset{\text{Carbonic oxide.}}{3CO}.$$

The potassic cyanide thus formed is then treated according to process No. 2.

4. By heating together an alcoholic solution of ammonia, chloroform, and potassic hydrate:—

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Chloroform.}}{CHCl_3} + 3KHo = 3KCl + \underset{\text{Hydrocyanic acid.}}{NCH} + 3OH_2.$$

Reactions.—1. Hydrocyanic acid in contact with water slowly passes, partly into ammonic oxalate as mentioned at p. 28, and partly into ammonic formate:—

$$\underset{\text{Hydrocyanic acid.}}{NCH} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Ammonic formate.}}{\left\{\begin{array}{l} H \\ CO(N^vH_4O). \end{array}\right.}$$

2. If hydrocyanic acid be mixed with concentrated hydrochloric acid, formic acid and ammonic chloride are produced:—

$$\underset{\text{Hydrocyanic acid.}}{NCH} + \underset{\text{Water.}}{2OH_2} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Formic acid.}}{\left\{\begin{array}{l} H \\ COHo \end{array}\right.} + \underset{\text{Ammonic chloride.}}{NH_4Cl}.$$

3. The displacement of the hydrogen in hydrocyanic acid by metals gives rise to a very extensive series of single and double cyanides. The following is a list of the most important of these compounds:—

Single Cyanides.

Potassic cyanide	KCy.
Zincic cyanide	$\mathbf{Zn}Cy_2$.
Cadmic cyanide	$\mathbf{Cd}Cy_2$.
Nickelous cyanide	$\mathbf{Ni}Cy_2$.
Argentic cyanide	$AgCy$.
Mercuric cyanide	$\mathbf{Hg}Cy_2$.
Aurous cyanide	$AuCy$.
Cuprous cyanide	$'\mathbf{Cu}'_2Cy_2$.
Ferrous cyanide	$\mathbf{Fe}Cy_2$.
Cobaltous cyanide	$\mathbf{Co}Cy_2$.

Double Cyanides.

Dipotassic zincic tetracyanide	K_2Zn'', Cy_4.
Dipotassic cadmic tetracyanide	K_2Cd'', Cy_4.
Dipotassic nickelous tetracyanide	K_2Ni'', Cy_4.
Potassic argentic dicyanide	KAg, Cy_2.
Potassic aurous dicyanide	KAu, Cy_2.
Potassic auric tetracyanide	KAu''', Cy_4.
Dipotassic cuprous tetracyanide	$K_2'Cu'_2, Cy_4$.
Dipotassic platinous tetracyanide	K_2Pt'', Cy_4.
Tetrapotassic diplatinic decacyanide	$K_4,'Pt'''_2Cy_{10}$.
Tetrapotassic ferrous hexacyanide. (Potassic ferrocyanide.)	$K_4, Fe''Cy_6$.
Hexapotassic diferric dodecacyanide. (Potassic ferricyanide.)	$K_6, 'Fe'''_2Cy_{12}$.
Hexapotassic dicobaltic dodecacyanide. (Potassic cobalticyanide.)	$K_6,'Co'''_2Cy_{12}$.
Hexapotassic dichromic dodecacyanide	$K_6,'Cr'''_2Cy_{12}$.
Hexapotassic dimanganic dodecacyanide	$K_6'Mn'''_2, Cy_{12}$.

The cyanides of the alkali metals when fused in contact with air, absorb oxygen, producing cyanates:—

$$\underset{\text{Potassic cyanide.}}{KCy} + O = \underset{\text{Potassic cyanate.}}{CyKo.}$$

Some of the single cyanides, as potassic cyanide, are readily decomposed by acids; others, as ferrous and aurous cyanides, may be boiled with moderately strong acids without decomposition.

Most of the insoluble single cyanides dissolve in solutions of the alkaline cyanides, forming double cyanides. Some of these double compounds, when acted upon by hydrochloric acid, evolve hydrocyanic acid, producing chlorides of both metals, as in the case of dipotassic zincic tetracyanide. These are called *easily decomposable cyanides*, and are indicated in the above Table by the comma being placed between the cyanogen and the metals.

Other double cyanides do not evolve hydrocyanic acid under the influence of hydrochloric acid, but produce a chloride of one of the metals, the remaining elements of the compound uniting with hydrogen to form a complex acid. In the above Table the double cyanides of this class are indicated by the comma being placed between the metals.

The most important of these double cyanides are the potassic ferrocyanide $K_4, Fe''Cy_6$, and the potassic ferricyanide $K_6, {}'Fe'''_2Cy_{12}$.

POTASSIC FERROCYANIDE.

$K_4, Fe''Cy_6$ or K_4Cfy.

Preparation.—1. By placing a mixture of iron filings and solution of potassic cyanide in contact with the air, oxygen is absorbed and potassic ferrocyanide produced:—

$$Fe + \underset{\text{Potassic cyanide.}}{6KCy} + \underset{\text{Water.}}{OH_2} + O = \underset{\text{Potassic ferrocyanide.}}{K_4Fe''Cy_6} + \underset{\text{Potassic hydrate.}}{2KHo.}$$

2. By digesting potassic cyanide with ferrous sulphide:—

$$\underset{\text{Ferrous sulphide.}}{FeS''} + \underset{\text{Potassic cyanide.}}{6KCy} = \underset{\text{Potassic ferrocyanide.}}{K_4Fe''Cy_6} + \underset{\text{Potassic sulphide.}}{SK_2.}$$

3. On a manufacturing scale it is prepared by fusing nitrogenous animal matter with potassic carbonate and iron filings

in iron vessels, lixiviating the resulting mass with water, and crystallizing.

Reactions.—1. Potassic ferrocyanide, when fused with potassic carbonate, forms potassic cyanide and cyanate:—

$$\underset{\text{Potassic ferrocyanide.}}{Fe''Cy_6K_4} + \underset{\text{Potassic carbonate.}}{COKo_2} = \underset{\text{Potassic cyanide.}}{5KCy} + \underset{\text{Potassic cyanate.}}{CyKo} + Fe + \underset{\text{Carbonic anhydride.}}{CO_2}.$$

2. By mixing solution of potassic ferrocyanide with ether and hydrochloric acid, hydroferrocyanic acid is precipitated:—

$$\underset{\text{Potassic ferrocyanide.}}{Fe''Cy_6K_4} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Potassic chloride.}}{4KCl} + \underset{\text{Hydroferrocyanic acid.}}{Fe''Cy_6H_4}.$$

3. Potassic ferrocyanide produces, with solutions of ferrous salts, a light-blue precipitate, which rapidly becomes dark blue in contact with the air:—

$$\underset{\text{Potassic ferrocyanide.}}{Fe''Cy_6K_4} + \underset{\text{Ferrous sulphate.}}{SO_2Feo''} = \underset{\text{Light-blue precipitate.}}{Fe''Cy_6Fe''K_2} + \underset{\text{Potassic sulphate.}}{SO_2Ko_2}.$$

4. With ferric salts it gives prussian blue:—

$$\underset{\text{Potassic ferrocyanide.}}{3Fe''Cy_6K_4} + \underset{\text{Ferric chloride.}}{2Fe_2Cl_6} = \underset{\text{Prussian blue.}}{3Fe''Cy_2, 2'Fe'''_2Cy_6} + \underset{\text{Potassic chloride.}}{12KCl}.$$

5. With cupric salts it gives a red precipitate of cupric ferrocyanide:—

$$\underset{\text{Potassic ferrocyanide.}}{K_4Fe''Cy_6} + \underset{\text{Cupric sulphate.}}{2SO_2Cuo''} = \underset{\text{Cupric ferrocyanide.}}{Cu''_2Fe''Cy_6} + \underset{\text{Potassic sulphate.}}{2SO_2Ko_2}.$$

POTASSIC FERRICYANIDE.

$K_6,'Fe'''_2Cy_{12}$ or K_6Cfdy.

Preparation.—By the action of oxidizing substances, such as chlorine or nitric acid, on potassic ferrocyanide:—

$$\underset{\text{Potassic ferrocyanide.}}{2K_4Fe''Cy_6} + Cl_2 = \underset{\text{Potassic ferricyanide.}}{K_6'Fe'''_2Cy_{12}} + \underset{\text{Potassic chloride.}}{2KCl}.$$

Reaction.—Potassic ferricyanide produces no precipitate with solutions of ferric salts, but causes a deep-blue precipitate with ferrous compounds:—

$$\underset{\text{Potassic ferricyanide.}}{K_6{}'Fe'''_2Cy_{12}} + \underset{\text{Ferrous sulphate.}}{3SO_2Feo''} = \underset{\text{Turnbull's blue.}}{Fe''_3{}'Fe'''_2Cy_{12}} + \underset{\text{Potassic sulphate.}}{3SO_2Ko_2}.$$

OTHER COMPOUNDS OF CYANOGEN.

There are two isomeric chlorides of cyanogen:—

$$\underset{\text{Gaseous.}}{CyCl.} \qquad \underset{\text{Solid.}}{Cy_3Cl_3.}$$

The molecular volume of both cyanic chlorides is □□.
1 *litre of vapour of liquid cyanic chloride weighs*.. 30·75 *criths*.
1 *litre of vapour of solid cyanic chloride weighs* 92·25 „

Liquid cyanic chloride solidifies at $-5°$, and boils at $15^{c}{\cdot}5$, whilst solid cyanic chloride fuses at 145°, and boils at 190°.

Cyanogen produces, with hydroxyl, three isomeric acids and an isomeric neutral body:—

Cyanic acid	$CyOH$ or $CyHo$.
Cyanuric acid (3 isomers)	$Cy_3O_3H_3$ or Cy_3Ho_3.
Fulminuric acid..........	$Cy_3O_3H_3$ or Cy_3Ho_3(?).
Cyamelide	$Cy_nO_nH_n$ or Cy_nHo_n.

When potassic cyanide is boiled with sulphur, the latter is dissolved and the solution contains potassic sulphocyanate:—

$$\underset{\text{Potassic cyanide.}}{CyK} + S = \underset{\text{Potassic sulphocyanate.}}{CyKs.}$$

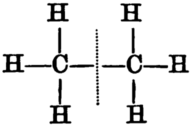
This compound produces with ferric salts a blood-red colour.

OXATYL.

$$\left\{\begin{array}{l}COHo\\COHo\end{array}\right.\cdot$$

This radical, in the isolated condition, constitutes dry oxalic acid; and in combination with hydrogen and other radicals it enters into the composition of nearly all organic acids. Acids containing one semimolecule of oxatyl are monobasic, those containing two are dibasic, and those containing three are tribasic.

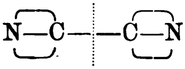
The relations between methyl, oxatyl, and cyanogen are very simple:—



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & \vdots & | & & \\ H & - & C & -\vdots- & C & - & H \\ & & | & \vdots & | & & \\ & & H & & H & & \end{array}$$

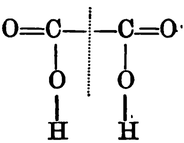
$\left\{\begin{array}{l} CH_3 \\ CH_3 \end{array}\right.$.

Methyl.



$\left\{\begin{array}{l} CN''' \\ CN''' \end{array}\right.$.

Cyanogen.



$$\begin{array}{ccccccc} O & = & C & -\vdots- & C & = & O \\ & & | & \vdots & | & & \\ & & O & \vdots & O & & \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

$\left\{\begin{array}{l} COHo \\ COHo \end{array}\right.$.

Oxatyl.

In methyl the two carbon atoms are united together by one bond of each, the remaining three bonds of each atom being saturated by three atoms of hydrogen. In cyanogen the carbon atoms are united in the same manner, but the three remaining bonds of each carbon atom are saturated by triad nitrogen; whilst in oxatyl the three remaining bonds are saturated with the dyad element oxygen and the monad radical hydroxyl.

Oxatyl has not been united with chlorine to produce oxatylic chloride (COHoCl); nor has its hydroxyl been replaced by chlorine to form $\left\{\begin{array}{l} COCl \\ COCl \end{array}\right.$. When treated with phosphoric chloride, it yields carbonic oxide and carbonic anhydride:—

$$\underset{\text{Oxatyl.}}{\left\{\begin{array}{l} COHo \\ COHo \end{array}\right.} + \underset{\substack{\text{Phosphoric} \\ \text{chloride.}}}{PCl_5} = \underset{\substack{\text{Carbonic} \\ \text{oxide.}}}{CO} + \underset{\substack{\text{Carbonic} \\ \text{anhydride.}}}{CO_2} + \underset{\substack{\text{Hydrochloric} \\ \text{acid.}}}{2HCl} + \underset{\substack{\text{Phosphoric} \\ \text{oxytrichloride.}}}{POCl_3}.$$

OXALIC ACID.

$$\left\{\begin{array}{l}COHo\\COHo\end{array}\right., 2OH_2 \text{ (crystallized).}$$

Occurrence.—In the form of the hydric potassic salt in *Oxalis acetosella*, and in the form of different salts in many other plants, and also in the animal organism.

Preparation.—1. From its elements through the medium of potassic cyanide. (See pp. 28 and 30.)

2. By passing carbonic anhydride over heated sodium :—

$$\begin{array}{ccccc} 2CO_2 & + & Na_2 & = & \left\{\begin{array}{l}CONao\\CONao\end{array}\right.. \\ \text{Carbonic anhydride.} & & & & \text{Sodic oxalate.}\end{array}$$

3. By the oxidation of a large number of organic compounds. Most organic substances are converted by oxidizing agents into oxalic acid before their final transformation into carbonic anhydride and water: thus sugar is transformed into oxalic acid by the action of nitric acid.

4. By heating sawdust with a mixture of potash and soda, oxalates of these bases are formed.

Transformations.—1. By the action of heat, oxalic acid is transformed into carbonic anhydride and oxatylic hydride, or formic acid :—

$$\begin{array}{ccccc} \left\{\begin{array}{l}COHo\\COHo\end{array}\right. & = & CO_2 & + & \left\{\begin{array}{l}H\\COHo\end{array}\right.. \\ \text{Oxalic acid.} & & \text{Carbonic anhydride} & & \text{Formic acid.}\end{array}$$

A portion of the formic acid is at the same time decomposed into water and carbonic oxide :—

$$\begin{array}{ccccc} \left\{\begin{array}{l}H\\COHo\end{array}\right. & = & OH_2 & + & CO. \\ \text{Formic acid.} & & \text{Water.} & & \text{Carbonic oxide.}\end{array}$$

2. Substances having a strong attraction for water, such as

sulphuric acid, transform oxalic acid into water, carbonic oxide, and carbonic anhydride:—

$$\underset{\text{Oxalic acid.}}{\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COHo}\end{matrix}\right.} = \underset{\text{Carbonic oxide.}}{\mathrm{CO}} + \underset{\text{Carbonic anhydride.}}{\mathrm{CO_2}} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

3. Heated with an excess of alkali, oxalic acid (or an oxalate) yields hydrogen and a carbonate:—

$$\underset{\text{Potassic oxalate.}}{\left\{\begin{matrix}\mathrm{COKo}\\ \mathrm{COKo}\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{\mathrm{2KHo}} = \underset{\text{Potassic carbonate.}}{\mathrm{2COKo_2}} + \mathrm{H_2}.$$

4. Argentic oxalate explodes when heated, producing silver and carbonic anhydride:—

$$\underset{\text{Argentic oxalate.}}{\left\{\begin{matrix}\mathrm{COAgo}\\ \mathrm{COAgo}\end{matrix}\right.} = \underset{\text{Carbonic anhydride.}}{\mathrm{2CO_2}} + \mathrm{Ag_2}.$$

Salts of Oxalic Acid.—Oxalic acid forms three series of salts:—

Normal.	Acid.	Superacid.
$\left\{\begin{matrix}\mathrm{COKo}\\ \mathrm{COKo}\end{matrix}\right..$	$\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COKo}\end{matrix}\right..$	$\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COKo}\end{matrix}\right., \left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COHo}\end{matrix}\right..$
$\left\{\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\right.\mathrm{Bao}''.$	$\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{CO}\\ \mathrm{Bao}''\\ \mathrm{CO}\\ \mathrm{COHo}\end{matrix}\right..$	

OXAMIC ACID.

$$\left\{\begin{matrix}\mathrm{CO(N'''H_2)}\\ \mathrm{COHo}\end{matrix}\right. \text{ or } \left\{\begin{matrix}\mathrm{COAd}\\ \mathrm{COHo}\end{matrix}\right..$$

Preparation.—By heating hydric ammonic oxalate to 230°:—

$$\underset{\text{Hydric ammonic oxalate.}}{\left\{\begin{matrix}\mathrm{CO(N^{v}H_4O)}\\ \mathrm{COHo}\end{matrix}\right.} = \underset{\text{Oxamic acid.}}{\left\{\begin{matrix}\mathrm{CO(N'''H_2)}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

Reaction.—By boiling oxamic acid with water it is retransformed into hydric ammonic oxalate.

OXAMIDE.

$$\left\{\begin{matrix}CO(N'''H_2)\\CO(N'''H_2)\end{matrix}\right. \text{ or } \left\{\begin{matrix}COAd\\COAd\end{matrix}\right..$$

Preparation.—1. By distilling normal ammonic oxalate:—

$$\underset{\text{Normal ammonic oxalate.}}{\left\{\begin{matrix}CO(N^{v}H_4O)\\CO(N^{v}H_4O)\end{matrix}\right.} = \underset{\text{Water.}}{2OH_2} + \underset{\text{Oxamide.}}{\left\{\begin{matrix}CO(N'''H_2)\\CO(N'''H_2)\end{matrix}\right.}.$$

2. By acting upon ethylic oxalate by ammonia:—

$$\underset{\text{Ethylic oxalate.}}{\left\{\begin{matrix}COEto\\COEto\end{matrix}\right.} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Oxamide.}}{\left\{\begin{matrix}CO(N'''H_2)\\CO(N'''H_2)\end{matrix}\right.} + \underset{\text{Alcohol.}}{2EtHo}.$$

Reactions.—1. Oxamide, when heated with phosphoric anhydride, evolves cyanogen:—

$$\underset{\text{Oxamide.}}{\left\{\begin{matrix}CO(N'''H_2)\\CO(N'''H_2)\end{matrix}\right.} = \underset{\text{Water.}}{2OH_2} + \underset{\text{Cyanogen.}}{\left\{\begin{matrix}CN'''\\CN'''\end{matrix}\right.}.$$

2. Dilute acids convert it into oxalic acid and ammonic salts:—

$$\underset{\text{Oxamide.}}{\left\{\begin{matrix}CO(N'''H_2)\\CO(N'''H_2)\end{matrix}\right.} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Oxalic acid.}}{\left\{\begin{matrix}COHo\\COHo\end{matrix}\right.}$$

$$+ \underset{\text{Ammonic sulphate.}}{SO_2(N^{v}H_4O)_2}.$$

By distilling the oxalates of the compound ammonias instead of ammonic oxalate, compound oxamides are obtained:—

$$\underset{\text{Methylammonic oxalate.}}{\left\{\begin{matrix}CO(N^{v}MeH_3O)\\CO(N^{v}MeH_3O)\end{matrix}\right.} = \underset{\text{Water.}}{2OH_2} + \underset{\text{Dimethyloxamide.}}{\left\{\begin{matrix}CO(N'''MeH)\\CO(N'''MeH)\end{matrix}\right.}.$$

$$\underset{\text{Phenylammonic oxalate.}}{\left\{\begin{matrix}CO(N^{v}PhH_3O)\\CO(N^{v}PhH_3O)\end{matrix}\right.} = \underset{\text{Water.}}{2OH_2} + \underset{\text{Diphenyloxamide.}}{\left\{\begin{matrix}CO(N'''PhH)\\CO(N'''PhH)\end{matrix}\right.}.$$

CHAPTER V.

HYDRIDES OF THE ORGANIC RADICALS.

This family is divided into two classes:—

Class I. Hydrides of the Positive Radicals.
Class II. Hydrides of the Negative Radicals.

Class I.

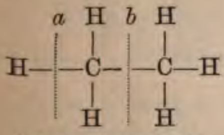
HYDRIDES OF THE POSITIVE RADICALS.

Two series of hydrides belonging to this class are well known; they are:—

1. Hydrides of the Radicals of the Methyl series.
2. Hydrides of the Radicals of the Phenyl series.

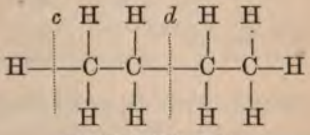
1. *HYDRIDES OF THE RADICALS OF THE METHYL SERIES, Marsh-gas or* C_nH_{2n+2} *Series.*

With the exception of the first member of the series—marsh-gas—these compounds are identical with the radicals of the methyl series. Thus methyl and ethylic hydride both contain C_2H_6, and ethyl and butylic hydride both contain C_4H_{10}. The graphic formulæ exhibit no difference between these pairs of bodies respectively. Thus:—



$$\begin{array}{ccccc} & a\;H & & b\;H & \\ & | & & | & \\ H- & -C- & & -C- & H \\ & | & & | & \\ & H & & H & \end{array}$$

Methyl or ethylic hydride.



$$\begin{array}{ccccccc} & c\;H & H & & d\;H & H & \\ & | & | & & | & | & \\ H- & -C- & C- & & -C- & C- & H \\ & | & | & & | & | & \\ & H & H & & H & H & \end{array}$$

Ethyl or butylic hydride.

These formulæ do not show us whether the molecule of methyl or ethylic hydride will separate at *a* and so be represented by the formula $\left\{\begin{matrix}\mathbf{C}(CH_3)H_2\\ H\end{matrix}\right.$, or at *b* and so be written thus, $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_3\end{matrix}\right.$; or whether the molecule of ethyl or butylic hydride will separate at *c*, and so be formulated $\left\{\begin{matrix}\mathbf{C}(C_3H_7)H_2\\ H\end{matrix}\right.$—or at *d*, when it should be represented by $\left\{\begin{matrix}\mathbf{C}(CH_3)H_2\\ \mathbf{C}(CH_3)H_2\end{matrix}\right.$.

A difference between methyl and ethylic hydride can only be conceived on the supposition that the four bonds of carbon have not equal values in combination, a hypothesis which is, however, not altogether unsupported by facts.

Preparation.—1. There is only one process of general application for preparing these hydrides; it consists in bringing water into contact with the zinc compounds of the respective radicals:—

$$\underset{\text{Zinc compound of radical.}}{\mathbf{Zn}(C_nH_{2n+1})_2} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Zincic hydrate.}}{\mathbf{Zn}Ho_2} + \underset{\text{Hydride of radical.}}{2\left\{\begin{matrix}C_nH_{2n+1}\\ H\end{matrix}\right.}.$$

The corresponding compounds containing more positive metals might doubtless be substituted for those of zinc.

2. There are several special processes which may be used for preparing these hydrides. Thus all the hydrides above that of methyl may be obtained, together with the corresponding dyad radical, by acting upon the iodide of the monad radical by zinc:—

$$\underset{\text{Iodide of the monad radical.}}{2\left\{\begin{matrix}C_nH_{2n+1}\\ I\end{matrix}\right.} + Zn = \underset{\text{Zincic iodide.}}{\mathbf{Zn}I_2} + \underset{\text{Dyad radical.}}{C_nH_{2n}} + \underset{\text{Hydride of monad radical}}{\left\{\begin{matrix}C_nH_{2n+1}\\ H\end{matrix}\right.}.$$

Methylic hydride, or marsh-gas, is produced during putrefaction, and by the distillation of potassic acetate with excess of potassic hydrate.

The destructive distillation of coal and of allied substances also furnishes a large number of the members of this series.

Character.—They are all distinguished by their great chemical indifference, and by their forming substitution compounds containing chlorine, bromine, &c.

The following list contains the hydrides of the monad radicals hitherto studied:—

		Boiling-points.
Methylic hydride, or Marsh-gas	MeH or $C\ H_4$	
Ethylic hydride	EtH or C_2H_6	
Propylic or tritylic hydride	PrH or C_3H_8	
Butylic or tetrylic hydride	BuH or C_4H_{10}	slightly above 0°
Amylic or pentylic hydride	AyH or C_5H_{12}	37—39°
Hexylic or caproylic hydride	CpH or C_6H_{14}	71·5
Heptylic hydride	C_7H_{16}	98·4
Octylic hydride	C_8H_{18}	124
Nonylic hydride	C_9H_{20}	136—138
Decatylic hydride	$C_{10}H_{22}$	160—162
Endecatylic hydride	$C_{11}H_{24}$	180—184
Dodecatylic hydride	$C_{12}H_{26}$	196—200
Tridecatylic hydride	$C_{13}H_{28}$	216—218
Tetradecatylic hydride	$C_{14}H_{30}$	236—240
Pentadecatylic hydride	$C_{15}H_{32}$	255—260

Of the members of this series higher than propylic hydride, various isomers are possible, of which a considerable number have been prepared. Thus there are two butylic hydrides—normal butylic hydride, $(\mathbf{C}PrH_2)H$, and tertiary butylic hydride, $\mathbf{C}Me_3H$. The hydrides enumerated in the above list are all normal. As has already been stated, the hydrides of the radicals are identical with the isolated radicals possessing the same molecular weight and the same constitution.

METHYLIC HYDRIDE, *Methane, Marsh-gas, Light Carburetted Hydrogen, Fire-damp.*

CH_4 or MeH.

Molecular weight = 16. *Molecular volume* ☐☐. 1 *litre weighs* 8 *criths.*

Occurrence.—1. As a product of the decomposition of organic substances out of contact with air.

2. Evolved in coal-mines.

3. The gas of the mud-volcano at Bulganak in the Crimea is nearly pure marsh-gas.

Preparation.—1. By the action of water on zincic methide. (See general reaction, p. 40.)

2. By distilling two parts of potassic acetate, two of potassic hydrate, and three of lime:—

$$\underset{\substack{\text{Potassic}\\\text{acetate.}}}{\left\{\begin{matrix}CH_3\\COKo\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\substack{\text{Potassic}\\\text{carbonate.}}}{COKo_2} + \underset{\substack{\text{Methylic}\\\text{hydride.}}}{CH_4}.$$

3. By the reduction of carbonic chloride or of chloroform with sodium amalgam and water:—

$$\underset{\substack{\text{Carbonic}\\\text{chloride.}}}{CCl_4} + 4H_2 = \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{4HCl} + \underset{\substack{\text{Methylic}\\\text{hydride.}}}{CH_4}:$$

$$\underset{\text{Chloroform.}}{CHCl_3} + 3H_2 = \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{3HCl} + \underset{\substack{\text{Methylic}\\\text{hydride.}}}{CH_4}.$$

4. By passing carbonic disulphide and hydrosulphuric acid, or carbonic disulphide and steam, over ignited copper:—

$$\underset{\substack{\text{Carbonic}\\\text{disulphide.}}}{CS''_2} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{2SH_2} + 8Cu = \underset{\substack{\text{Cuprous}\\\text{sulphide.}}}{4'Cu'_2S''} + \underset{\substack{\text{Methylic}\\\text{hydride.}}}{CH_4}.$$

5. By the action of the electric discharge on a mixture of carbonic oxide and hydrogen:—

$$\underset{\substack{\text{Carbonic}\\\text{oxide.}}}{CO} + 3H_2 = \underset{\substack{\text{Methylic}\\\text{hydride.}}}{CH_4} + \underset{\text{Water.}}{OH_2}.$$

6. By the destructive distillation of organic substances, such as wood and coal.

Reactions.—1. When equal volumes of methylic hydride and chlorine are exposed to diffused daylight, methylic chloride is formed:—

$$\underset{\substack{\text{Methylic}\\\text{hydride.}}}{CH_4} + Cl_2 = \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl} + \underset{\substack{\text{Methylic}\\\text{chloride.}}}{CH_3Cl}.$$

2. When methylic hydride is passed through a red-hot

tube, hydrogen, ethylene, acetylene, and ethylic hydride are produced.

ETHYLIC HYDRIDE, *Ethane.*

C_2H_6 or $CMeH_3$.

Molecular weight = 30. *Molecular volume* □□. 1 *litre weighs* 15 *criths. Liquefies at* 1° *under a pressure of about* 50 *atmospheres.*

Preparation.—1. By the action of water on zincic ethide (see p. 40).

2. By the action of ethylic iodide on sodic ethide, ethylene being simultaneously produced:—

$$\underset{\text{Sodic ethide.}}{CMeH_2Na} + \underset{\text{Ethylic iodide.}}{CMeH_2I} = \underset{\text{Sodic iodide.}}{NaI} + \underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Ethylic hydride.}}{CMeH_3}.$$

Reactions.—1. When equal volumes of ethylic hydride and chlorine are exposed to diffused daylight, the following action takes place:—

$$\underset{\text{Ethylic hydride.}}{CMeH_3} + Cl_2 = \underset{\text{Ethylic chloride.}}{CMeH_2Cl} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

2. When a mixture of two volumes of chlorine and one of ethylic hydride is exposed to the action of diffused daylight ethylidenic dichloride is formed:—

$$\underset{\text{Ethylic hydride.}}{CMeH_3} + 2Cl_2 = \underset{\text{Ethylidenic dichloride.}}{CMeHCl_2} + \underset{\text{Hydrochloric acid.}}{2HCl}.$$

AMYLIC HYDRIDE, *Pentane.*

C_5H_{12} or $CBuH_3$.

Molecular weight = 72. *Molecular volume* □□. 1 *litre of amylic hydride vapour weighs* 36 *criths. Boils at* 37—39°.

Occurrence.—In petroleum and coal-oil.

Preparation.—By digesting zinc and amylic iodide with water or alcohol at 100°:—

$$\underset{\substack{\text{Amylic}\\ \text{iodide.}}}{2\mathbf{C}\mathrm{BuH_2I}} + 2\mathrm{Zn} + \underset{\text{Water.}}{2\mathbf{O}\mathrm{H_2}} = \underset{\substack{\text{Amylic}\\ \text{hydride.}}}{2\mathbf{C}\mathrm{BuH_3}}$$

$$+ \underset{\substack{\text{Zincic}\\ \text{hydrate.}}}{\mathrm{ZnHo_2}} + \underset{\substack{\text{Zincic}\\ \text{iodide.}}}{\mathrm{ZnI_2}}.$$

PARAFFIN.

C_nH_{2n+2}.

This body is produced, together with numerous other compounds of a like nature, by the destructive distillation of boghead coal and similar substances. It is also found in petroleum and asphalt. Chlorine has no action upon paraffin in the cold; but if it be passed into melted paraffin, the latter is slowly attacked, hydrochloric acid being evolved. In this reaction paraffin resembles the hydrides of the monad radicals, and differs from the dyad radicals, to which class it was formerly considered to belong. In the formula C_nH_{2n+2} for paraffin, the value of n has not yet been satisfactorily determined; in fact it is probable that several distinct hydrides of the class now under consideration are confounded under this name.

II. *HYDRIDES OF THE RADICALS OF THE PHENYL SERIES.*

Before proceeding to describe in detail the hydrides of the phenyl or benzene series of radicals, it will be necessary, in order that the laws of isomerism governing this group of compounds may be understood, to give some account of the views held by chemists with regard to the constitution of benzene and its derivatives. At the same time, as the methods by which the theory of the benzene series has been elaborated afford an excellent example of the successful application of the study of chemical reactions to the solution of an exceedingly complex problem of constitution, the subject may be here treated with what might otherwise seem a disproportionate minuteness.*

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* The line of proof here followed is borrowed, with some alterations, from Ladenburg's *Theorie der aromatischen Verbindungen.*

The benzene series, sometimes also distinguished as the aromatic series, includes at the present moment, partly owing to its richness in isomers and partly to the attention which has been devoted to it of late years, almost as large a number of compounds as all the other series taken together. All these so-called aromatic compounds may be regarded as derived from the hydrocarbon benzene, $\mathbf{C}_6H_6$, by the replacement of one or more atoms of hydrogen by atoms of various other monad elements or by atomic groups. In fact, many of these compounds may be synthetically prepared in this way; and, in cases where this is not possible, benzene may be obtained from the compounds by appropriate reactions. The cluster of atoms C_6, which forms the foundation of the benzene compounds, is distinguished as the *nucleus;* the substituted groups are termed *lateral* groups—sometimes *lateral chains.* A chain of atoms, attached with both its ends to the benzene nucleus, is known as a *closed lateral chain.* Hydrogen atoms directly attached to the C_6 group are referred to as *hydrogen of the nucleus*, in order to distinguish them from *hydrogen of the lateral groups.* No benzene compound can contain less than six atoms of carbon.

Three circumstances have combined to facilitate the study of the derivatives of benzene: the extreme stability of the nucleus C_6, the atoms of which seldom undergo separation except under the action of very powerful oxidising agents; the mobility of the hydrogen atoms, rendering them readily exchangeable for other atoms or groups, and distinguishing this hydrocarbon in the most marked manner from the inert hydrocarbons of the C_nH_{2n+2} series; and lastly, the mobility of many of these substituted groups and the multiplicity of the reactions by which they may, when necessary, be again replaced by hydrogen or directly exchanged for other groups or atoms.* In all these substitutions it is assumed that the substituted atom or group holds exactly the same position with regard to the rest of the molecule as was held by the displaced atom or group—in other words, that the same bond or bonds which are rendered vacant by the exit of the latter, are satisfied on the entrance of the former; and that only in very exceptional cases does an intramolecular migration, or shifting of the relative positions of the atoms within the molecule, occur. On this supposition, without the aid of which most of the phenomena of organic chemistry would be inexplicable, all speculations with regard to constitution are based.

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* Most of the reactions to which it will be necessary to refer in the course of the following proof will probably be somewhat unintelligible to the student at the present stage. He will be able to verify them, how-

There are two conditions, deducible from the reactions of benzene, which every constitutional formula of this hydrocarbon must fulfil, and which have the effect of limiting the number of possible formulæ to two. Of these two formulæ, one is eliminated by its failure to fulfil certain other conditions, the nature of which will be explained further on. These two conditions are:—

1. The six hydrogen atoms of benzene are interequivalent.

2. For each hydrogen atom there are among the other hydrogen atoms two distinct pairs, the members of each of which are interequivalent in relation to this particular atom.

By the *interequivalence* of two or more hydrogen atoms in a molecule is understood the fact that when any one of their number is replaced by a particular atom or group of atoms, the same compound is produced, no matter which of the interequivalent atoms is so replaced. The theory of bonds explains this by the supposition that the interequivalent atoms are all connected, both directly and indirectly, in exactly the same manner with the rest of the molecule—in other words, *interequivalent atoms are in equiposition.*

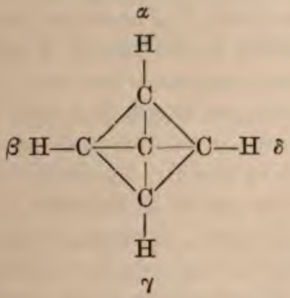
---

ever, by reference to other parts of this work. Most of the corresponding general reactions will be found under nitrobenzene, aniline, and diazo-compounds.

Two or more hydrogen atoms in a molecule are said to be interequivalent in relation to a particular hydrogen atom, when, after first replacing this hydrogen atom by a different atom or group, the relatively interequivalent atoms may each in turn be replaced by any given atom or group with the production in each case of the same compound. In order that this may be so, it is necessary not only that the various relatively interequivalent atoms should be in equiposition with regard to the molecule as a whole, but that they should be in equiposition with regard to this particular hydrogen atom.

This is generally expressed by saying that they are situated *symmetrically* in relation to this hydrogen atom.

These points will be most readily rendered clear by an illustration. In a compound of the formula—



the hydrogen atoms α, β, γ and δ, are in equiposition, and consequently interequivalent. Further, α and γ are symmetrical, and consequently interequivalent, in relation to δ, and also to β; but α and β are unsymmetrical, and therefore not interequivalent, in relation to δ.

The proof of the existence of the two above-mentioned conditions in benzene will be given in three stages :—

A. Interequivalence of four hydrogen atoms.

B. Relative interequivalence of two distinct pairs of hydrogen atoms towards a fifth hydrogen atom.

C. Interequivalence of all six hydrogen atoms.

A. *Interequivalence of Four Hydrogen Atoms in Benzene.*—Phenol, $\mathbf{C}_6H_5Ho$, a compound derived from benzene by the substitution of a semimolecule of hydroxyl for one atom of hydrogen, is converted by treatment with phosphoric bromide into monobrombenzene, $\mathbf{C}_6H_5Br$, the hydroxyl group being replaced by bromine. By the joint action of sodium and carbonic anhydride, the bromine of monobrombenzene is in its turn replaced by oxatyl, yielding benzoic acid, $\mathbf{C}_6H_5(COHo)$. The hydroxyl group in phenol and the oxatyl group in benzoic acid thus replace in benzene the same hydrogen atom, which may be distinguished as *a*. From benzoic acid three isomeric oxyacids—salicylic acid, oxybenzoic acid, and paraoxybenzoic acid—all of the general formula $\mathbf{C}_6H_4Ho(COHo)$, in which a hydroxyl group is substituted for an atom of hydrogen in the nucleus of benzoic acid, may be obtained by appropriate reactions. The isomerism of these three acids is explained according to the theory of bonds by the supposition that in these compounds the hydroxyl group replaces three different hydrogen atoms *b*, *c*, and *d*, which are not symmetrically situated in relation to the atom *a*, the place of which is occupied by oxatyl. By distillation with lime, the oxatyl of these three acids is replaced by hydrogen, and three phenols are obtained. A careful study of the properties of these three phenols has shown their absolute identity with ordinary phenol, the substance which formed the starting point of the above series of reactions. It is therefore immaterial which of these four hydrogen atoms of benzene, *a*, *b*, *c*, and *d*, is replaced by hydroxyl: the same compound is produced in each case; and the four atoms are consequently interequivalent.

B. *Relative Interequivalence of Two Distinct Pairs of Hydrogen Atoms in Benzene towards a Fifth Hydrogen Atom.*—*α. First Pair.*—Metabrombenzoic acid, $\mathbf{C}_6H_4Br(COHo)$, obtained by the action of bromine on benzoic acid, yields, when treated with nitric acid, two isomeric nitrobrombenzoic acids, $\mathbf{C}_6H_3Br(NO_2)(COHo)$. When these two acids are treated with reducing agents, the nitro-group $\mathbf{N}O_2$ is converted into the amido-group $\mathbf{N}H_2$, whilst at the same time the bromine is replaced by hydrogen, and both acids yield *the same* amidobenzoic acid, $\mathbf{C}_6H_4(NH_2)(COHo)$. From this follows the existence of one pair of hydrogen atoms relatively interequivalent towards the hydrogen atom replaced by oxatyl in benzoic acid. For if one brombenzoic acid can yield two nitrobrombenzoic acids, this can be explained only on the assumption that the nitro-group has replaced two different hydrogen atoms a and b,* as in the formula—

$$\overset{a}{\mathbf{C}_6H_3Br(NO_2)(COHo)},$$

and—

$$\overset{b}{\mathbf{C}_6H_3Br(NO_2)(COHo)}.$$

In order that the two amidobenzoic acids—

$$\overset{a}{\mathbf{C}_6H_4(NH_2)(COHo)},$$

and—

$$\overset{b}{\mathbf{C}_6H_4(NH_2)(COHo)},$$

obtained from these by reduction may be identical, it is necessary that the hydrogen atoms a and b should be relatively interequivalent towards the hydrogen atom which has been replaced by oxatyl.

β. Second Pair.—When salicylic acid, $\mathbf{C}_6H_4Ho(COHo)$, is treated with nitric acid, two isomeric nitrosalicylic acids, $\mathbf{C}_6H_3Ho(NO_2)(COHo)$, are obtained. In each of these the hydroxylic hydrogen may be replaced by ethyl, yielding two isomeric ethereal salts, $\mathbf{C}_6H_3Eto(NO_2)(COEto)$, which on treatment with ammonia yield two corresponding nitramidobenzamides, $\mathbf{C}_6H_3Ad(NO_2)(COAd)$. These are converted by the action of caustic alkalies into two nitramidobenzoic acids, $\mathbf{C}_6H_3Ad(NO_2)(COHo)$. Both of these isomeric acids, when treated with nitrous anhydride and alcohol, in order to replace the amido-group by hydrogen, yield the same nitrobenzoic acid. This is possible only on the assumption that there are two hydrogen atoms relatively interequivalent towards the hydrogen atom which has been replaced by oxatyl. For if two isomeric nitrosalicylic acids can be obtained from salicylic acid, the nitro-group must replace two different hydrogen atoms *a* and *b*—

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* It need scarcely be said that the letters employed to distinguish various hydrogen atoms in one proof have nothing to do with those employed in another proof.

$$\overset{a}{\mathbf{C}_6H_3Ho(NO_2)(COHo)},$$

and

$$\overset{b}{\mathbf{C}_6H_3Ho(NO_2)(COHo)};$$

and in order that, when the hydroxyl-group has been replaced by hydrogen (which is the result of the above series of reactions), the nitrobenzoic acids,

$$\overset{a}{\mathbf{C}_6H_4(NO_2)(COHo)}$$

and

$$\overset{b}{\mathbf{C}_6H_4(NO_2)(COHo)}$$

may be identical, it is necessary that the hydrogen atoms *a* and *b* should be relatively interequivalent towards the hydrogen atom which has been replaced by oxatyl. Further, this pair is distinct from the pair the existence of which was first proved; inasmuch as this nitrobenzoic acid yields on reduction an amidobenzoic acid (meta-amidobenzoic acid), which is quite distinct from that (ortho-amidobenzoic acid) which was obtained from the two nitrobrombenzoic acids.

The existence of two distinct pairs of hydrogen atoms relatively interequivalent towards a fifth hydrogen atom has thus been proved.

C. *Interequivalence of all Six Hydrogen Atoms in Benzene.*—Under *A* the interequivalence of four hydrogen atoms in benzene was proved by showing that the three phenols obtained from the three oxybenzoic acids were identical with ordinary phenol. At the same time it was shown that phenol could be converted into benzoic acid, and that therefore the same hydrogen atom *a*, which is replaced in phenol by the hydroxyl-group, is occupied in benzoic acid by oxatyl. The hydroxyl-groups in the three oxybenzoic acids replace three different hydrogen atoms, *b*, *c*, and *d*. Of these three no two must be relatively interequivalent towards *a*, otherwise two of the oxybenzoic acids would be identical. Now, as it has been shown that there are two independent pairs of hydrogen atoms relatively interequivalent towards this very hydrogen atom *a*, there are only two atoms, *e* and *f*, remaining to form with two of the above three (*b*, *c*, and *d*) these two pairs. If, therefore, the two atoms, *e* and *f*, were in turn replaced by hydroxyl (the atom *a* being still replaced by oxatyl) two oxybenzoic acids would be obtained identical with two of those already known. It follows further from this that the phenols in which the hydroxyl-group replaces the atoms *e* and *f* are identical with ordinary phenol, and the six hydrogen atoms of benzene are therefore interequivalent.

As all these hydrogen atoms are interequivalent the same conditions hold for all of them, and each has therefore its two distinct pairs relatively interequivalent towards it.

These two laws form the basis of the benzene theory, and from them the laws of isomerism of the benzene compounds can be derived. Thus, as all the hydrogen atoms are interequivalent, only one monosubstitution-compound is possible. For the same reason, only one pentasubstitution-compound is possible, when only one kind of atom or group is substituted. It also follows that all bisubstitution-compounds can exist in three isomeric modifications. For representing by *a*, *b*, *c*, *d*, *e*, *f*, the six atoms to be replaced, and indicating by brackets the pairs relatively interequivalent towards *a* :—

$$a,\quad \underbrace{b,\quad c,}\quad \underbrace{d,\quad e,}\quad f$$

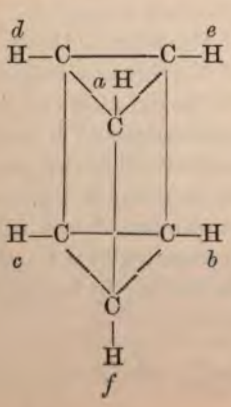
we have the bisubstitution-compounds:—

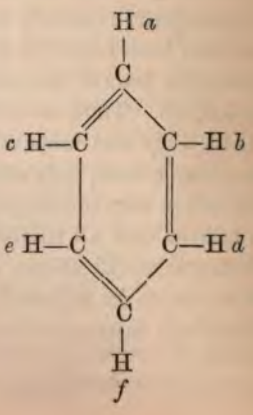
1. $ab = ac$.
2. $ad = ae$.
3. af.

There is no doubt that, by the mathematical discussion of these laws of symmetry, it would be possible to deduce the laws of isomerism of even the most complex substitution-compounds without reference to any definite graphic formula.

The experimental facts are in thorough accordance with the above theory. No case is known of a monosubstitution-compound of benzene existing in two isomeric forms and none of a bisubstitution-compound in more than three. Isolated results, which seemed to contradict these laws, have either been withdrawn by the authors themselves or have been disproved by later observers.

Graphic Formula of Benzene.—By systematically exhausting all the possible graphic combinations corresponding to the empirical formula C_6H_6, it is found that only two graphic formulæ satisfy the required conditions—equiposition of all six hydrogen atoms and symmetry of two distinct pairs of hydrogen atoms towards a fifth hydrogen atom. These two formulæ are:—

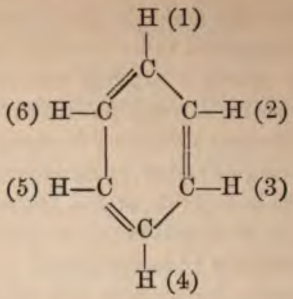




The first of these formulæ is the "prism" formula of Ladenburg. It is supposed to be viewed in perspective in the figure, the carbon atoms occupying the corners of a three-sided prism. It satisfies in every particular the above requirements: the six hydrogen atoms are in equiposition and there are two distinct pairs, *bc* and *de*, symmetrically placed in relation to *a*. But this formula is not in harmony with the known constitution of naphthalene, a higher derivative of benzene (see constitution of naphthalene).

The second formula for benzene was originally suggested as a hypothesis by Kekulé at a time when the experimental data, from which the above limiting conditions are deduced, did not exist. This formula has been generally accepted by chemists. It has, however, one weak point. The hydrogen atoms are in equiposition, but the condition of the two symmetrical pairs is not fulfilled: *b* and *c* are not symmetrical toward *a*, nor are, strictly considered, *d* and *e*. The bisubstitution-compound *ab* would be different from *ac;* and, in case two dissimilar substituting atoms or groups were employed, *ad* would differ from *ae*. The result would be that benzene ought to yield respectively four and five bisubstitution-compounds, according as the substituting atoms or groups are similar or dissimilar. This difficulty can only be got over by aid of the further hypothesis that in a closed chain the influence of double and single bonds disappears. We therefore make the *assumption* (in violation certainly of our definition of the relative interequivalence of two atoms towards a third) that *ab is* identical with *ac* and *ad* with *ae*. In this form the formula explains the existence of all known derivatives of benzene.

Localization of the Lateral Groups.—By arbitrarily selecting as a starting-point any one hydrogen atom in the benzene hexagon (as Kekulé's formula is sometimes termed—the word *hexagon* being understood to refer entirely to the graphic formula, and in no way to the molecule itself) and numbering the other hydrogen atoms in their order, thus :—



a system is arrived at by means of which the relations of the various polysubstitution-compounds of benzene may be denoted. Thus, in the bisubstitution-compounds there are the three positions, 1 : 2, 1 : 3, and 1 : 4, and the compounds in which the lateral groups hold these positions are distinguished in nomenclature as *ortho*-, *meta*-, and *para*-compounds respectively. The trisubstitution-compounds are distinguished as 1 : 2 : 4 orthopara, 1 : 3 : 4 metapara, &c., and so on with the higher compounds.

It becomes a matter of very great theoretical interest to be able to assign to each of the various benzene derivatives its proper place in the above classes. This problem, the *localization of the lateral groups*, may be divided into two distinct parts. For example, in the bisubstitution-compounds it is necessary first to find some means of determining the relative positions for three such compounds belonging to the three different classes and then by utilising the ease with which one lateral group may be replaced by another, to transform these into other bisubstitution-compounds, or to transform other bisubstitution-compounds into these, and thus to refer all the bisubstitution-compounds to these three. In this way three parallel series are obtained, the position of each of which is determined by that of one standard compound. Fortunately, however, there is more than one set of standard compounds, and nearly all the transformations have been effected in more than one way. The concordant results which have been obtained by these independent methods afford the best proof of the correctness of the theory.

The localization of the lateral groups in one set of standard compounds may be arrived at as follows :—

1. The amidobenzoic acid obtained in the proof of the first symmetrical pair (see p. 49) yields on treating with nitrous anhydride and boiling with water—by which means the amido-group is replaced by hydroxyl—salicylic acid. The second amidobenzoic acid, in which the amido-group replaces one of the hydrogen atoms of the second symmetrical pair (p. 50) yields on similar treatment oxybenzoic acid. One of these two acids, salicylic acid and oxybenzoic acid, must therefore correspond to the position $1:2=1:6$, whilst in the other the position is $1:3=1:5$—these being the two pairs of symmetrical positions. There remains, therefore, for the third, so-called paraoxybenzoic acid, only the position $1:4$. The para-position is therefore proved for one compound.*

2. By the action of dehydrating agents upon acetone, mesitylene—a trimethylbenzene—is obtained :—

$$\underset{\text{Acetone.}}{3\mathbf{C}\mathbf{O}(CH_3)_2} = \underset{\text{Mesitylene.}}{\mathbf{C}_6H_3(CH_3)_3} + \underset{\text{Water.}}{3\mathbf{O}H_2}$$

By the oxidation of mesitylene, a tribasic acid of the formula, $\mathbf{C}_6H_3(COHo)_3$, is obtained, which, when distilled with lime, yields benzene, thus proving that mesitylene is a trimethylbenzene. By a series of ingeniously selected reactions, the general principle of which is similar to that employed in the proof of the symmetrical pairs, it may be shown that mesitylene yields the same substitution-compound, no matter which of the three hydrogen atoms of the nucleus is replaced by a given atom or group. These three hydrogen atoms are therefore interequivalent, and must therefore be symmetrically arranged in the graphic formula, a condition which can be satisfied only in the following manner:—

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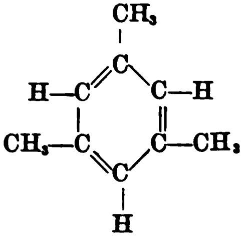
* It must be carefully borne in mind that the proofs given in this chapter for the localization of the lateral groups are not dependent for their validity upon the adoption of any particular graphic formula for benzene. They apply quite as well to Ladenburg's formula as to Kekulé's, and would apply to any other formula (if such a formula existed) in which the same conditions of symmetry were satisfied. Viewed in this light, graphic formulæ generally are nothing more than convenient geometrical devices, which, by expressing interequivalence and relative interequivalence in terms of geometrical symmetry, render it possible to predict cases of isomerism in substitution-compounds. Symmetry, in two substitution-compounds derived from the same compound and containing the same substituted atoms or groups, denotes identity; lack of symmetry, isomerism. As already stated, any graphic formula which correctly performs this work of translation—and there may be several such formulæ for one compound—will correctly predict the cases of isomerism.



The three methyl-groups are therefore in the position 1 : 3 : 5. By replacing any one of these groups by hydrogen a dimethylbenzene in which the methyl-groups are in the position 1 : 3—metadimethylbenzene—is obtained. This compound may be shown by means of various transformations, to belong to the same series as oxybenzoic acid, which must therefore be regarded as meta-oxybenzoic acid.

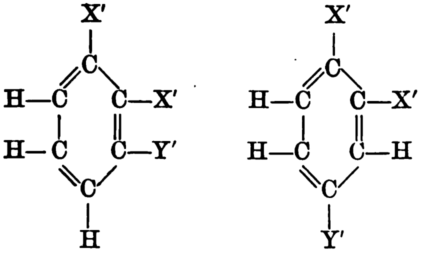
3. In paraoxybenzoic acid the position is 1 : 4; in metaoxybenzoic acid it is 1 : 3 = 1 : 5; and there therefore remains for salicylic acid—the third oxybenzoic acid—only the ortho-position, 1 : 2 = 1 : 6.

These three standard compounds are therefore:—

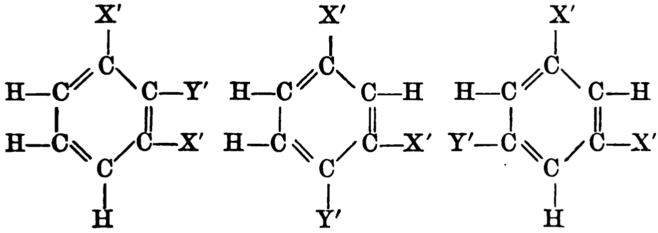
	Fusing-point.
Salicylic acid, $C_6H_4(\overset{1}{C}OHo)\overset{2}{H}o$	155—156°
Metaoxybenzoic acid, $C_6H_4(\overset{1}{C}OHo)\overset{3}{H}o$ ..	200
Paraoxybenzoic acid, $C_6H_4(\overset{1}{C}OHo)\overset{4}{H}o$ ..	210

In another set of standard compounds the lateral groups may be localized by a totally different method. Starting with three isomeric bisubstitution-compounds, in which the substituted atoms or groups are both of one kind, and substituting a third atom or group different from the others, it will be seen that the ortho-bisubstitution-compound ought to yield two trisubstitution-compounds; the meta-compound, three; and the para-compound, only one. Thus, if the two similar atoms or groups be represented by X′ and the dissimilar atom or group by Y′, there would be—

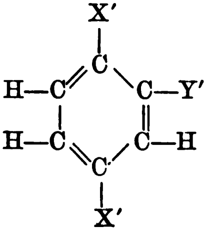
From the Ortho-compound.



From the Meta-compound.



From the Para-compound.



Now there are six diamidobenzoic acids known. In these the amido-groups will correspond to the X′, and the oxatyl-groups to Y′, in the above formulæ. On distilling these six diamidobenzoic acids with lime in order to replace the oxatyl by hydrogen, it is found that *two* of them yield a diamidobenzene fusing at 102°; *three* others, a diamidobenzene fusing at 63°; whilst *one* yields a third diamidobenzene fusing at 147°. From this it follows that in the first of these diamidobenzenes the amido-groups are in the position 1 : 2; in the second, in the position 1 : 3; and in the third, in the position 1 : 4.

There are other methods, which need not be described here, of localizing the lateral groups. As has been already mentioned, all these methods yield concordant results.

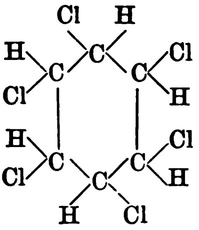
The above methods of localization have been extended to the various higher substitution-compounds of benzene. Much has already been done in this direction, but large gaps still remain to be filled up.

The following is a list of the number of isomers which the formula predicts for each substitution-compound of benzene when the substituted atoms or groups are all similar:—

Mono-	substitution-	compounds	1 compound.
Di-	,,	,,	3 isomers
Tri-	,,	,,	3 ,,
Tetra-	,,	,,	3 ,,
Penta-	,,	,,	1 compound
Hexa-	,,	,,	1 ,,

In the case of the chlorbenzenes, all of these nine compounds are known, and the relative position of the chlorine atoms in each has been determined.

Benzene also forms addition compounds. Thus there is a benzene hexachloride of the formula—



the double bonds having been converted into single bonds in taking up six atoms of chlorine.

The following list includes the principal members of the hydrides of the radicals of the phenyl series :—

Homologous series.	Name.	Formula.	Boiling-point.
C_6H_6	Benzene	C_6H_6	80·5°
C_7H_8	Toluene (methylbenzene)	C_6H_5Me	111
C_8H_{10}	Xylene—		
	Orthoxylene (dimethylbenzene)	$C_6H_4Me_2$ (1 : 2)	140—141
	Metaxylene (dimethylbenzene)	$C_6H_4Me_2$ (1 : 3)	137
	Paraxylene (dimethylbenzene)	$C_6H_4Me_2$ (1 : 4)	136—137
	Ethylbenzene	C_6H_5Et	134
C_9H_{12}	Cumene—		
	Mesitylene (trimethylbenzene)	$C_6H_3Me_3$ (1 : 3 : 5)	163
	Pseudocumene (trimethylbenzene)	$C_6H_3Me_3$ (1 : 3 : 4)	166
	Ethylmethylbenzene	C_6H_4EtMe (1 : 4)	161—162
	Propylbenzene	C_6H_5Pr	157
	Isopropylbenzene	$C_6H_5\beta Pr$	151
$C_{10}H_{14}$	Cymene—		
	Durene (tetramethylbenzene)	$C_6H_2Me_4$(1:2:4:5)	190

Homologous series.	Name.	Formula.	Boiling-point.
$C_{10}H_{14}$	Cymene—		
	Methylmesitylene (tetramethylbenzene)	$C_6H_2Me_4(1:2:3:5)$	192—194°
	Ethyldimethylbenzene	$C_6H_3EtMe_2(1:3:5)$	180—182
	Diethylbenzene	$C_6H_4Et_2\ (1:4)$	179
	Propylmethylbenzene	$C_6H_4PrMe\ (1:4)$	175—176
	Isopropylmethylbenzene	$C_6H_4\beta PrMe\ (1:4)$	171—172
	Butylbenzene	C_6H_5Bu	180
$C_{11}H_{16}$	Amylbenzene	C_6H_5Ay	193
$C_{12}H_{18}$	Hexamethylbenzene	C_6Me_6	260

Preparation.—1. These hydrides are produced by the distillation with excess of calcic or potassic hydrate of the alkaline salts of the acids containing the same positive radicals:—

$$\begin{array}{ccccccc} \left\{\begin{matrix} C_nH_{2n-7} \\ COKo \end{matrix}\right. & + & KHo & = & COKo_2 & + & \left\{\begin{matrix} C_nH_{2n-7} \\ H \end{matrix}\right. \\ \text{Potassic salt.} & & \text{Potassic hydrate.} & & \text{Potassic carbonate.} & & \text{Hydride of radical.} \end{array}$$

2. In addition to benzene, the following hydrides containing methyl-groups are formed in the destructive distillation of coal and other organic substances:—toluene, the three xylenes, mesitylene, and pseudocumene. These are all obtained from coal-tar by fractional distillation. No member of this series containing as a lateral chain ethyl, or any radical of the C_nH_{2n+1} series higher than methyl, has been found in coal-tar.

3. Ethylbenzene is prepared by the action of sodium upon a mixture of ethylic bromide and monobrombenzene:—

$$\begin{array}{ccccccccc} C_6H_5Br & + & EtBr & + & Na_2 & = & C_6H_5Et & + & 2NaBr \\ \text{Monobrombenzene.} & & \text{Ethylic bromide.} & & & & \text{Ethyl benzene.} & & \text{Sodic bromide.} \end{array}$$

Toluol may be synthesised in the same manner, substituting methylic for ethylic bromide.

The formation of mesitylene from acetone has already been described (p. 55).

Isopropylbenzene, the hydrocarbon to which the name cumene was originally applied, is formed as in reaction (1) by distilling cuminic acid (paraisopropylbenzoic acid), $\mathbf{C}_6H_4\beta Pr(COHo)$ (1 : 4) obtained from oil of cumin, with caustic lime.

Parapropylmethylbenzene, the first cymene discovered, is contained in oil of Roman cumin. It may be prepared synthetically by the action of sodium on a mixture of parabromtoluol, C_6H_4BrMe (1 : 4), and propylic iodide (Reaction 3). It is most readily obtained from camphor.

Hexamethylbenzene is prepared by the catalytic action of aluminic chloride on a solution of methylic chloride in benzene:—

$$\underset{\text{Benzene.}}{\mathbf{C}_6H_6} + \underset{\text{Methylic chloride.}}{6MeCl} = \underset{\text{Hexamethylbenzene.}}{\mathbf{C}_6Me_6} + \underset{\text{Hydrochloric acid.}}{6HCl.}$$

The aluminic chloride apparently undergoes no change:—

Law of oxidation of the Hydrocarbons derived from Benzene.—When these hydrocarbons are treated with oxidizing agents the nucleus remains as a rule intact, and the lateral chains, no matter how many carbon atoms they may contain, are oxidized away, only one carbon atom of each chain remaining attached to the nucleus in the form of oxatyl. The rule, therefore, is:—*A hydrocarbon of the benzene series containing* n *lateral chains yields on oxidation an* n*-basic acid of benzene.* Thus toluene, ethylbenzene, and amylbenzene, all yield benzoic acid. Paraxylene, paraethylmethylbenzene, and parapropylmethylbenzene yield terephthalic acid. Hexamethylbenzene yields mellitic acid, $\mathbf{C}_6(COHo)_6$. By partial oxidation of a hydrocarbon containing two or more lateral chains one lateral chain may be converted into oxatyl, whilst the others are left unattacked. Thus from paradiethylbenzene paraethylbenzoic acid may be obtained. In such a case the lateral chain which is richest in carbon atoms is attacked first. Thus paraethylmethylbenzene yields paramethylbenzoic (paratoluic) acid. The following equations will serve as examples :—

$$\underset{\text{Paradiethyl-benzene.}}{\mathbf{C}_6\mathrm{H}_4\mathrm{Et}_2} + 6\mathrm{O}_2 = \underset{\text{Terephthalic acid (1 : 4).}}{\mathbf{C}_6\mathrm{H}_4(\mathrm{COHo})_2} + 2\mathbf{C}\mathrm{O}_2 + 4\mathbf{O}\mathrm{H}_2.$$

$$\underset{\text{Paradiethyl-benzene.}}{\mathbf{C}_6\mathrm{H}_4\mathrm{Et}_2} + 3\mathrm{O}_2 = \underset{\text{Paraethyl-benzoic acid.}}{\mathbf{C}_6\mathrm{H}_4\mathrm{Et}(\mathrm{COHo})} + \mathbf{C}\mathrm{O}_2 + 2\mathbf{O}\mathrm{H}_2.$$

Chromic acid is the best oxidizing agent in the case of meta- and para-compounds, but it cannot be employed with ortho-compounds, as it oxidizes these completely to carbonic anhydride and water. However, by oxidizing with potassic permanganate in neutral or in alkaline solution, or with dilute nitric acid, the ortho-compounds may be converted into their corresponding acids. Thus orthoxylene yields orthomethylbenzoic (orthotoluic) acid, $\mathbf{C}_6\mathrm{H}_4\mathrm{Me}(\mathrm{COHo})(1:2)$, and ultimately phthalic acid, $\mathbf{C}_6\mathrm{H}_4(\mathrm{COHo})_2\ (1:2)$.

Properties.—These hydrides are distinguished from those of the radicals of the $\mathrm{C}_n\mathrm{H}_{2n+1}$ series by being less indifferent to chemical agents.

The halogens can replace by their direct action hydrogen atoms either of the nucleus or of the lateral groups, and the two series of compounds thus formed possess totally distinct properties. Chlorine, for example, which is attached to the nucleus, as in chlorbenzene, $\mathbf{C}_6\mathrm{H}_5\mathrm{Cl}$, or chlortoluene, $\mathbf{C}_6\mathrm{H}_4\mathrm{Cl}(\mathrm{CH}_3)$, is in a condition of so stable combination that it cannot be removed by caustic alkalies or silver salts; whereas, when the chlorine belongs to a lateral group, as in benzylic chloride, $\mathbf{C}_6\mathrm{H}_5(\mathrm{CH}_2\mathrm{Cl})$, an isomer of chlortoluene, it may readily be exchanged by double decomposition for other atoms or groups, thus behaving like chlorine in the $\mathrm{C}_n\mathrm{H}_{2n+2}$ series.

A peculiar law holds with regard to the direct substitution of chlorine or bromine in the homologues of benzene. For example, in the case of toluol, by the action of chlorine or bromine in the cold, or in presence of iodine or molybdic pentachloride (even when heated), the substitution of chlorine or bromine takes place in the nucleus; but by acting on boiling toluol alone, hydrogen of the lateral group is replaced.

By treatment with strong nitric acid these hydrides yield nitro-compounds, in which hydrogen of the nucleus is replaced by one or more nitro-groups. Thus benzene yields nitrobenzene, $\mathbf{C}_6H_5(N^vO_2)$. From toluene a mixture of ortho- and paranitrotoluene is obtained. The ortho-compound is a liquid boiling at 222—223°; paranitrotoluene is a crystalline solid fusing at 54°. These nitrotoluenes are converted by oxidation into the corresponding nitrobenzoic acids. Most of the higher members of the series yield mixtures of isomeric nitro-compounds. By the action of reducing agents the nitro-group is converted into the amido-group $\mathbf{N}H_2$: thus nitrobenzene yields aniline, $\mathbf{C}_6H_5(NH_2)$; orthonitrotoluene forms orthotoluidine, $\mathbf{C}_6H_4Me(NH_2)$ (1 : 2).

When these hydrides are treated with strong sulphuric acid one or more atoms of hydrogen of the nucleus are replaced by the monad group $(\mathbf{S}O_2Ho)$. The compounds so formed are termed sulphonic acids. Thus benzene yields benzenesulphonic acid:—

$$\begin{array}{ccccccc} \mathbf{C}_6H_6 & + & \mathbf{S}O_2Ho_2 & = & \mathbf{C}_6H_5(SO_2Ho) & + & \mathbf{O}H_2. \\ \text{Benzene.} & & \text{Sulphuric acid.} & & \text{Benzene-sulphonic acid.} & & \text{Water.} \end{array}$$

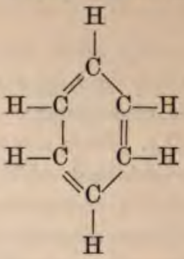
With toluene a mixture of ortho- and paratoluenesulphonic acids is obtained, $\mathbf{C}_6H_4Me(SO_2Ho)$ (1:2) and $\mathbf{C}_6H_4Me(SO_2Ho)$ (1 : 4).

Neither the nitro-compounds nor the sulphonic acids of the hydrides of the C_nH_{2n+1} series of radicals can be prepared by direct reactions.

By the reducing action of hydriodic acid at high temperatures the C_nH_{2n-6} series is converted into the C_nH_{2n+2} series. Thus benzene yields a hydride, $\mathbf{C}_6H_{14}$.

BENZENE, *Benzol, Phenylic Hydride.*

$\mathbf{C}_6H_6$ or PhH.



Molecular weight = 78. *Molecular volume* □□. 1 *litre of benzene vapour weighs* 39 *criths. Fuses at* 3°. *Boils at* 80°·5.

Occurrence.—In Rangoon petroleum and in coal-tar.

Preparation.—1. By heating with an excess of lime or baryta any acid of benzene which contains no lateral groups except oxatyl:—

$$\underset{\text{Benzoic acid.}}{\left\{\begin{matrix}\mathbf{C}_6H_5\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Lime.}}{\mathbf{C}aO} = \underset{\text{Benzene.}}{\left\{\begin{matrix}\mathbf{C}_6H_5\\ H\end{matrix}\right.} + \underset{\text{Calcic carbonate.}}{\mathbf{C}OCao''}.$$

$$\underset{\text{Phthalic acid.}}{\mathbf{C}_6H_4(\mathbf{C}OHo)_2} + 2\mathbf{C}aO = \underset{\text{Benzene.}}{\mathbf{C}_6H_6} + 2\mathbf{C}OCao''.$$

$$\underset{\text{Mellitic acid.}}{\mathbf{C}_6(\mathbf{C}OHo)_6} + 6\mathbf{C}aO = \underset{\text{Benzene.}}{\mathbf{C}_6H_6} + 6\mathbf{C}OCao''.$$

2. By heating the vapour of benzoic acid to redness, when it splits up into benzene and carbonic anhydride:—

$$\underset{\text{Benzoic acid.}}{\mathbf{C}_6H_5(\mathbf{C}OHo)} = \underset{\text{Carbonic anhydride.}}{\mathbf{C}O_2} + \underset{\text{Benzene.}}{\mathbf{C}_6H_6}.$$

3. By heating acetylene to low redness:—

$$\underset{\text{Acetylene.}}{3'''\mathbf{C}'_2H_2} = \underset{\text{Benzene.}}{\mathbf{C}_6H_6}.$$

4. By the destructive distillation of coal.

5. In small quantity, when many organic substances,—fats, vapour of acetic acid or alcohol, &c.,—are passed through a red-hot tube.

SUBSTITUTION DERIVATIVES OF BENZENE.

Chloro-Compounds.

MONOCHLORBENZENE, *Phenylic Chloride.*

Boils at 132°.

Preparation.—1. By the action of chlorine on boiling benzene, or on benzene in which a small quantity of iodine is dissolved:—

$$\underset{\text{Benzene.}}{\mathbf{C}_6H_6} + Cl_2 = \underset{\text{Monochlorbenzene.}}{\mathbf{C}_6H_5Cl} + \underset{\text{Hydrochloric acid.}}{HCl.}$$

2. By treating phenol with phosphoric chloride:—

$$\underset{\text{Phenol.}}{\mathbf{C}_6H_5Ho} + \underset{\text{Phosphoric chloride.}}{\mathbf{P}Cl_5} = \underset{\text{Monochlorbenzene.}}{\mathbf{C}_6H_5Cl} + \underset{\text{Phosphoric oxytrichloride.}}{\mathbf{P}OCl_3} + \underset{\text{Hydrochloric acid.}}{HCl.}$$

3. From diazobenzene chloroplatinate by distillation with sodic carbonate (see p. 69).

Higher Chlorine Compounds.

By the prolonged action of chlorine upon benzene the various higher stages of chlorination up to hexachlorbenzene are obtained. The following is a complete list of all the chlorine substitution derivatives of benzene, and includes every theoretically possible isomer. Some of the isomers have been obtained only by indirect reactions:—

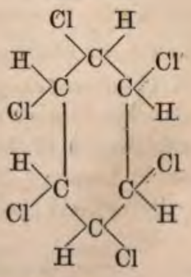
	State of aggregation.	Fusing-point.	Boiling-point.	Sp. gr.
Monochlorbenzene, $\mathbf{C}_6H_5Cl$	Liquid	−40°	132°	1·128
Dichlorbenzene, $\mathbf{C}_6H_4Cl_2$ (1 : 2)	Liquid	—	179	1·328
” ” (1 : 3)	Liquid	—	172	1·307
” ” (1 : 4)	Solid	56	173	—

	State of aggregation.	Fusing-point.	Boiling-point.	p. gr
Trichlorbenzene, $C_6H_3Cl_3$ (1:2:3)	Solid	53°	218°	—
” ” (1:2:4)	Solid	17	213	—
” ” (1:3:5)	Solid	63·5	208	—
Tetrachlorbenzene, $C_6H_2Cl_4$, ... (1 : 2 : 3 : 4)	Solid	46	254	—
Tetrachlorbenzene, $C_6H_2Cl_4$, .. . (1 : 2 : 3 : 5)	Solid	51	246	—
Tetrachlorbenzene, $C_6H_2Cl_4$, ... (1 : 2 : 4 : 5)	Solid	138	243—246	—
Pentachlorbenzene, C_6HCl_5	Solid	86	276	—
Hexachlorbenzene, C_6Cl_6	Solid	222—226	332	—

A very convenient form of nomenclature applicable to isomeric benzene substitution derivatives containing only one kind of substituted atoms or groups, consists in classing together the compounds (1 : 4), (1 : 3 : 5), and (1 : 2 : 4 : 5), as *symmetrical;* (1 : 3), (1 : 2 : 4), and (1 : 2 : 3 : 5), as *unsymmetrical;* and (1 : 2), (1 : 2 : 3), and (1 : 2 : 3 : 4), as *adjacent*. The principle on which these names are chosen may be readily seen by referring to the graphic formulæ of the compounds.

BENZENE HEXACHLORIDE.

$C_6H_6Cl_6$.



Preparation.—By the direct union of chlorine and benzene when exposed to sunlight. It is also formed when chlorine is passed into boiling benzene:—

$$\underset{\text{Benzene.}}{C_6H_6} + 3Cl_2 = \underset{\text{Benzene hexachloride.}}{C_6H_6Cl_6}.$$

Reaction.—When heated it is decomposed into hydrochloric acid and unsymmetrical trichlorbenzene (1 : 2 : 4):—

$$\underset{\text{Benzene hexachloride.}}{C_6H_6Cl_6} = \underset{\text{Trichlorbenzene.}}{C_6H_3Cl_3} + \underset{\text{Hydrochloric acid.}}{3HCl}.$$

Bromo-, Iodo- and Fluo-compounds.

The bromo-compounds greatly resemble the corresponding chloro-compounds. All those predicted by theory have been prepared, with the exception of adjacent tetrabrombenzene.

The iodo-compounds have been less thoroughly investigated.

Fluobenzene, C_6H_5F, a crystalline solid, fusing at 40° and boiling at 180°, has been prepared.

Nitro-compounds.

The following have been produced:—

	Fusing-point.	Boiling-point.
Nitrobenzene, $C_6H_5(N^vO_2)$	3°	205°
Dinitrobenzene, $C_6H_4(N^vO_2)_2$ (1 : 2) ..	118	—
,, ,, (1 : 3) ..	90	—
,, ,, (1 : 4) ..	172	—
Trinitrobenzene, $C_6H_3(N^vO_2)_3$	121—122	—

NITROBENZENE.

$C_6H_5(N^vO_2)$ or $N^v(C_6H_5)O_2$.

Molecular weight = 123. *Molecular volume* ☐☐. 1 *litre of nitrobenzene vapour weighs* 61·5 *criths. Fuses at* 3°. *Boils at* 205°.

Preparation.—By the action of cold concentrated nitric acid on benzene:—

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{NO_2Ho} = \underset{\text{Nitrobenzene.}}{C_6H_5(N^vO_2)} + \underset{\text{Water.}}{OH_2}$$

Reactions.—1. By the action of reducing or hydrogenating agents, as zinc and hydrochloric acid, sulphuretted hydrogen, acetic acid and iron, stannous chloride or potassic arsenite, nitrobenzene is converted into the base aniline:—

$$\underset{\text{Nitrobenzene.}}{\mathbf{C}_6H_5(\mathbf{N}^vO_2)} + 3H_2 = \underset{\text{Aniline.}}{\mathbf{C}_6H_5(NH_2)} + \underset{\text{Water.}}{2\mathbf{O}H_2}.$$

2. By the action of sodium amalgam and water, nitro-benzene is converted into azobenzene, and finally into hydrazobenzene:—

$$\underset{\text{Nitrobenzene.}}{2\mathbf{N}^v(C_6H_5)O_2} + 4H_2 = \underset{\text{Azobenzene.}}{{}''\left\{\begin{matrix}\mathbf{N}(C_6H_5)\\ \mathbf{N}(C_6H_5)\end{matrix}\right.} + \underset{\text{Water.}}{4\mathbf{O}H_2}.$$

$$\underset{\text{Azobenzene.}}{{}''\left\{\begin{matrix}\mathbf{N}(C_6H_5)\\ \mathbf{N}(C_6H_5)\end{matrix}\right.} + H_2 = \underset{\text{Hydrazobenzene.}}{\left\{\begin{matrix}\mathbf{N}(C_6H_5)H\\ \mathbf{N}(C_6H_5)H\end{matrix}\right.}\cdot$$

Hydrazobenzene, when brought in contact with acids, does not form salts, but undergoes a peculiar intramolecular change, and is converted into the base benzidine:—

$$\left\{\begin{matrix}\mathbf{N}(C_6H_5)H\\ \mathbf{N}(C_6H_5)H\end{matrix}\right. = \left\{\begin{matrix}\mathbf{C}_6H_4(NH_2)\\ \mathbf{C}_6H_4(NH_2)\end{matrix}\right.$$

The amido-groups in benzidine are both in the para-position with regard to the point of union of the two nuclei.

DIAZO-COMPOUNDS.

DIAZOBENZENE.

$$''\left\{\begin{matrix}\mathbf{N}(C_6H_5)\\ \mathbf{N}Ho\end{matrix}\right. ?$$

Preparation.—Free diazobenzene has not been prepared in a state of purity, but its salts may be readily obtained. The nitrate is formed when nitrous anhydride is passed into a cooled solution of aniline nitrate:—

$$\underset{\substack{\text{Aniline}\\ \text{nitrate.}}}{2\left\{\begin{matrix}\mathbf{N}(C_6H_5)H_3\\ O\\ \mathbf{N}O_2\end{matrix}\right.} + \underset{\substack{\text{Nitrous}\\ \text{anhydride.}}}{\mathbf{N}_2O_3} = \underset{\substack{\text{Diazobenzene}\\ \text{nitrate.}}}{2\,{}''\left\{\begin{matrix}\mathbf{N}(C_6H_5)\\ \mathbf{N}\\ O\\ \mathbf{N}O_2\end{matrix}\right.} + \underset{\text{Water.}}{3\mathbf{O}H_2}.$$

Properties and Reactions.—The great importance of the diazo-compounds lies in the readiness with which the nitrogen attached to the nucleus may be replaced by various other atoms and groups. As nearly all aromatic amido-compounds yield diazo-compounds, these reactions have proved invaluable in solving the problems of the localization of the lateral groups.

1. By boiling diazobenzene nitrate with water, the nitrogen group is replaced by hydroxyl:—

$$\underset{\text{Diazobenzene nitrate.}}{\left\{\begin{array}{l}''\mathbf{N}'_2(C_6H_5)\\ O\\ \mathbf{N}O_2\end{array}\right.} + \underset{\text{Water.}}{OH_2} = \underset{\text{Phenol.}}{C_6H_5Ho} + N_2 + \underset{\text{Nitric acid.}}{\mathbf{N}O_2Ho}.$$

2. By boiling diazobenzene sulphate with alcohol, the nitrogen group is replaced by hydrogen, the alcohol being at the same time converted into aldehyde:—

$$\underset{\text{Diazobenzene sulphate.}}{\left\{\begin{array}{l}''\mathbf{N}'_2(C_6H_5)\\ O\\ \mathbf{S}O_2Ho\end{array}\right.} + \underset{\text{Alcohol.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{array}\right.} = \underset{\text{Benzene.}}{\mathbf{C}_6H_6} + N_2 + \underset{\text{Aldehyde.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OH\end{array}\right.} + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2}.$$

3. When diazobenzene sulphate is treated with hydriodic or hydrofluoric acid, the nitrogen group is replaced by the halogen atom:—

$$\underset{\text{Diazobenzene sulphate.}}{\left\{\begin{array}{l}''\mathbf{N}'_2(C_6H_5)\\ O\\ \mathbf{S}O_2Ho\end{array}\right.} + \underset{\text{Hydriodic acid.}}{HI} = \underset{\text{Iodobenzene (phenylic iodide).}}{\mathbf{C}_6H_5I} + N_2 + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2}.$$

4. By the dry distillation of diazobenzene chloroplatinate with sodic carbonate, the nitrogen group is replaced by chlorine:—

$$\underset{\text{Diazobenzene chloroplatinate.}}{[''\mathbf{N}'_2(C_6H_5)Cl_2]_2\mathbf{Pt}Cl_4} = \underset{\text{Chlorobenzene (phenylic chloride).}}{2\mathbf{C}_6H_5Cl} + Pt + 2Cl_2 + N_2.$$

The liberated chlorine is taken up by the alkali.

5. By distilling diazobenzene perbromide with lime, the nitrogen group is replaced by bromine :—

$$''N'_2(C_6H_5)Br,Br_2 \quad = \quad C_6H_5Br \quad + \quad Br_2 \quad + \quad N_2.$$

Diazobenzene perbromide. Brombenzene (phenylic chloride).

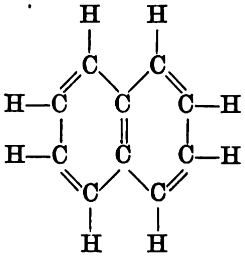
The lime takes up the liberated bromine.

HYDRIDES OF RADICALS CONTAINING COMPOUND BENZENE NUCLEI.

	Formula.	Fusing-point.	Boiling-point.
Naphthalene	$C_{10}H_8$	79·2°	218°
Phenanthrene......	$C_{14}H_{10}$	100	340
Anthracene........	$C_{14}H_{10}$	213	Above 360

NAPHTHALENE.

$C_{10}H_8$.



Molecular weight = 128. *Molecular volume* □□. 1 *litre of naphthalene vapour weighs* 64 *criths. Fuses at* 79°·2. *Boils at* 218°.

Occurrence.—In coal-tar.

Preparation.—1. By passing the vapour of phenylbutylene dibromide through a tube filled with lime heated to low redness :—

$$\left\{\begin{array}{l} C(C_6H_5)H_2 \\ CH_2 \\ CHBr \\ CH_2Br \end{array}\right. \quad = \quad C_{10}H_8 \quad + \quad 2HBr \quad + H_2.$$

Phenylbutylene dibromide. Naphthalene. Hydrobromic acid.

2. By the destructive distillation of coal.

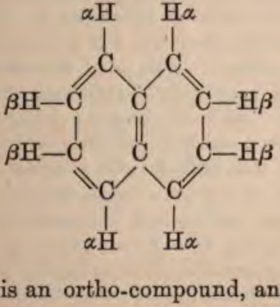
3. In small quantity when the vapour of many organic substances—alcohol, acetic acid, turpentine, &c.—is passed through a red-hot tube.

Properties and Constitution.—Naphthalene yields with chlorine, nitric acid, sulphuric acid and other reagents, substitution derivatives corresponding to those of benzene.

The constitution of naphthalene is determined in the following manner:—By the action of nitric acid on naphthalene, nitro-naphthalene, $C_{10}H_7(N^{v}O_2)$, is formed, and, from this, amidonaphthalene, $C_{10}H_7(NH_2)$, is obtained by reduction. On oxidation the amidonaphthalene yields phthalic acid, $C_6H_4(COHo)_2$ (1 : 2), and may therefore be formulated, $C_6H_4[C_4H_3(NH_2)]''$. The nitro-compound will then be—$C_6H_4[C_4H_3(N^{v}O_2)]''$: that is to say, there is a benzene nucleus present which does not contain the nitro-group. But by oxidizing this nitronaphthalene, nitrophthalic acid—

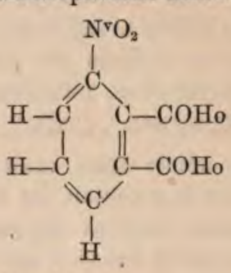
$$C_6H_3(N^{v}O_2)(COHo)_2,$$

is obtained, and therefore there must also be a benzene nucleus present, which does contain the nitro-group. As the molecule of naphthalene contains only ten atoms of carbon, the above conditions can be satisfied only on the supposition that it consists of two benzene nuclei having two carbon atoms in common, as in the formula—



As phthalic acid is an ortho-compound, and as naphthalene yields this acid, no matter which half of the molecule is oxidized, the two carbon atoms common to the two nuclei must be in the ortho-position.*

According to this constitutional formula, there ought to be two monosubstitution compounds of naphthalene possible, according as one of the four hydrogen atoms α, adjacent to the points of union of the two nuclei, or one of the four hydrogen atoms β, one place removed from the points of union, is replaced. As a fact, two parallel series of monosubstitution derivatives are known, and it is possible, as in the benzene group, to pass from one member of a series to another of the same series by means of diazo-reactions (p. 69). The localization of the substituted groups is very simply accomplished. The nitronaphthalene above mentioned (fusing-point 61°) yields on oxidation a nitrophthalic acid of the formula—



and is therefore α-nitrophthalene.

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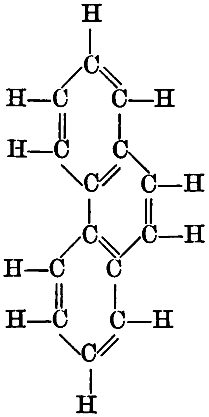
* Some chemists reverse this argument, making the production of phthalic acid by the oxidation of either half of the naphthalene molecule a proof (a "geometrical proof" as it is sometimes called) that phthalic acid is an ortho-compound. This proof is, however, faulty. By representing the benzene nucleus by Ladenburg's formula (p. 52), it is possible to construct two nuclei having two carbon atoms either in the meta- or in the para-position in common, and we should thus have a "geometrical proof" that phthalic acid is either a meta- or a para-compound. As, however, it can be independently proved that phthalic acid is an ortho-compound, and as it is impossible to construct two Ladenburg's "prisms" having two carbon atoms in the ortho-position in common, Ladenburg's formula fails in its application to naphthalene, and, as has already been shown (p. 52), there is no other formula besides Kekulé's remaining for our acceptance.

β-Nitrophthalene is not known, but α-nitronaphthalene can be converted into α-amidonaphthalene, and then, by the diazo-reaction, into α-chlornaphthalene, a liquid boiling at 254°, identical with one of the two known chlornaphthalenes. The remaining chlornaphthalene, a solid fusing at 61°, must therefore be the β compound.

PHENANTHRENE.

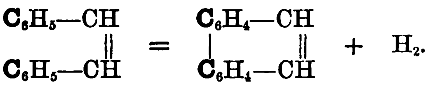
$C_{14}H_{10}$.



Molecular weight = 178. *Molecular volume* □□· 1 *litre of phenanthrene vapour weighs* 89 *criths. Fuses at* 100°. *Boils at* 340°.

Occurrence.—In coal-tar.

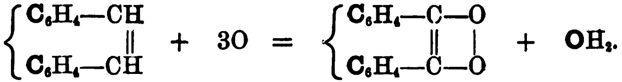
Preparation.—1. By passing stilbene (symmetrical diphenyl-ethylene) through a red-hot tube:—



$$\begin{matrix} C_6H_5\text{—}CH \\ \| \\ C_6H_5\text{—}CH \end{matrix} = \begin{matrix} C_6H_4\text{—}CH \\ | \qquad \| \\ C_6H_4\text{—}CH \end{matrix} + H_2.$$

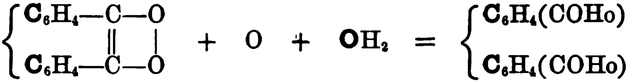
2. By the destructive distillation of coal.

Reaction.—On oxidation phenanthrene yields successively phenanthrenequinone, diphenic acid, and phthalic acid:—



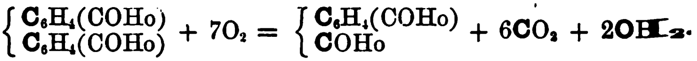
$$\left\{\begin{array}{l} C_6H_4-CH \\ \qquad\quad \| \\ C_6H_4-CH \end{array}\right. + 3O = \left\{\begin{array}{l} C_6H_4-C-O \\ \qquad\quad \|\ \ \ | \\ C_6H_4-C-O \end{array}\right. + OH_2.$$

Phenanthrene. Phenanthrene-quinone. Water.



$$\left\{\begin{array}{l} C_6H_4-C-O \\ \qquad\quad \|\ \ \ | \\ C_6H_4-C-O \end{array}\right. + O + OH_2 = \left\{\begin{array}{l} C_6H_4(COHo) \\ \\ C_6H_4(COHo) \end{array}\right.$$

Phenanthrene-quinone. Water. Diphenic acid. (1 : 2) (1 : 2).



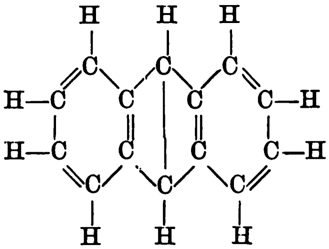
$$\left\{\begin{array}{l} C_6H_4(COHo) \\ C_6H_4(COHo) \end{array}\right. + 7O_2 = \left\{\begin{array}{l} C_6H_4(COHo) \\ COHo \end{array}\right. + 6CO_2 + 2OH_2.$$

Diphenic acid. Phthalic acid (1 : 2). Carbonic anhydride. Water.

Phenanthrene consists of three benzene nuclei, of which one shares four carbon atoms with the two others—two atoms with each. It may therefore be regarded as derived from naphthalene by a repetition of the process by which this hydrocarbon is derived from benzene.

ANTHRACENE.

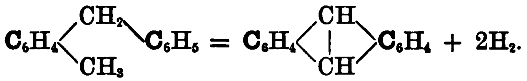
$C_{14}H_{10}$.



Molecular weight = 178. *Molecular volume* □□. 1 *litre of anthracene vapour weighs* 89 *criths. Fuses at* 213°. *Boils above* 360°.

Occurrence.—In coal-tar.

Preparation.—1. By passing orthobenzyltoluol through a red-hot tube :—

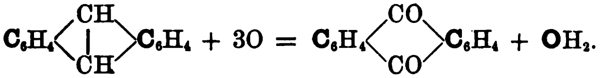


$$C_6H_4\left\langle\begin{matrix}CH_2\\ CH_3\end{matrix}\right. C_6H_5 = C_6H_4\left\langle\begin{matrix}CH\\ |\\ CH\end{matrix}\right\rangle C_6H_4 + 2H_2.$$

Benzyltoluol. (1 : 2). Anthracene.

2. By the destructive distillation of coal.

Reaction.—By oxidation, anthracene yields anthraquinone:—



$$C_6H_4\left\langle\begin{matrix}CH\\ |\\ CH\end{matrix}\right\rangle C_6H_4 + 3O = C_6H_4\left\langle\begin{matrix}CO\\ CO\end{matrix}\right\rangle C_6H_4 + OH_2.$$

Anthracene. Anthraquinone.

Three monosubstitution derivatives of anthracene are theoretically possible, and with this the facts, as far as they are known, are in accordance.

Class II.

HYDRIDES OF NEGATIVE RADICALS.

Only two of these are known:—

Cyanic hydride or Hydrocyanic acid.
Oxatylic hydride or Formic acid.

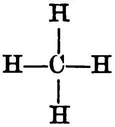
The first has already been considered (p. 29), and the second will be more conveniently studied in connexion with the fatty acids.

CHAPTER VI.

THE ALCOHOLS.

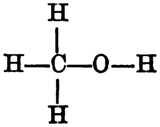
The alcohols form one of the most important of the families of organic compounds. The simplest member of this family is methylic alcohol, which is derived from marsh-gas by the substitution of one semimolecule of hydroxyl for one of hydrogen.

CH_4.



Marsh-gas.

CH_3Ho.



Methylic alcohol.

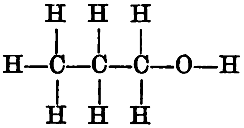
The alcohols have been termed the hydrated oxides of the positive radicals; but this is erroneous, as they do not contain water. They may more correctly be defined as the compounds of hydroxyl with the positive organic radicals, whence it follows that each series of positive radicals forms a corresponding series of alcohols. The alcohols act upon and saturate acids, forming a family of compounds termed *ethereal salts*. The acidity or acid-saturating powder of the alcohols depends upon the number of semimolecules of hydroxyl which they contain: the monad radicals give monohydric alcohols, or alcohols containing only one semimolecule of hydroxyl, the dyad radicals, dihydric alcohols, &c. We have thus the annexed three principal subdivisions of the alcohol family.

Monohydric.	Dihydric.	Trihydric.
Methyl or $C_nH_{2+1}Ho$ series.	Glycol or $C_nH_{2n}Ho_2$ series.	Glycerin or $C_nH_{2n-1}Ho_3$ series.
Vinyl, Allyl or $C_nH_{2n-1}Ho$ series.	Orcin or $C_nH_{2n-8}Ho_2$ series.	Pyrogallic or $C_nH_{2n-9}Ho_3$ series.
Phenyl or $C_nH_{2n-7}Ho$ series.		

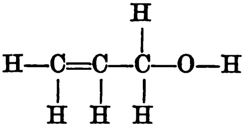
The following symbolic and graphic formulæ will exemplify the disposal of the bonds in these three subdivisions:—

Monohydric Alcohols.

$$\left.\begin{matrix}\text{Propylic alcohol.}\\ (\textit{Methyl series.})\end{matrix}\right\} = C_3H_7Ho \text{ or } \left\{\begin{matrix}C(CH_3)H_2\\ CH_2Ho\end{matrix}\right. .$$

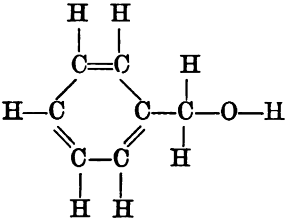


Allylic alcohol. (*Vinyl series.*) $\Big\}$ = C_3H_5Ho or $\left\{\begin{array}{l}C(CH_2)''H\\ CH_2Ho\end{array}\right.$.



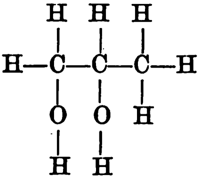
$$\begin{array}{ccccccccccc} & & & & & & H & & & & \\ & & & & & & | & & & & \\ H & - & C & = & C & - & C & - & O & - & H \\ & & | & & | & & | & & & & \\ & & H & & H & & H & & & & \end{array}$$

Benzylic alcohol. (*Phenyl series.*) $\Big\}$ = C_7H_7Ho or $\left\{\begin{array}{l}C_6H_5\\ CH_2Ho\end{array}\right.$.



Dihydric Alcohols.

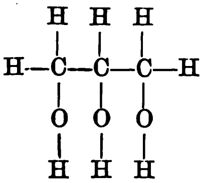
Propylenic alcohol, or propylic glycol . . . . $\Big\}$ = $C_3H_6Ho_2$ or $\left\{\begin{array}{l}C(CH_3)HHo\\ CH_2Ho\end{array}\right.$.



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & O & & O & & H & & \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

Trihydric Alcohols.

Glycerin . . . . = $C_3H_5Ho_3$ or $\left\{\begin{array}{l}CH_2Ho\\ CHHo\\ CH_2Ho\end{array}\right.$.



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & O & & O & & O & & \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

MONOHYDRIC ALCOHOLS:

Methyl or $C_nH_{2n+1}Ho$ series.

These alcohols may be divided into three classes :—

1. Monohydric normal alcohols $\left\{\begin{array}{l}\mathbf{C}(\mathrm{C}_n\mathrm{H}_{2n+1})\mathrm{H}_2\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$.
2. ,, secondary ,, $\left\{\begin{array}{l}\mathbf{C}(\mathrm{C}_n\mathrm{H}_{2+1}\mathrm{H}_2)\\ \mathbf{C}(\mathrm{C}_m\mathrm{H}_{2m+1})\mathrm{HHo}\end{array}\right.$.
3. ,, tertiary ,, $\left\{\begin{array}{l}\mathbf{C}(\mathrm{C}_n\mathrm{H}_{2n+1})\mathrm{H}_2\\ \mathbf{C}(\mathrm{C}_m\mathrm{H}_{2m+1})_2\mathrm{Ho}\end{array}\right.$.

In the general formula of the normal alcohols n may $= 0$, and even the whole radical $\mathbf{C}(\mathrm{C}_n\mathrm{H}_{2n+1})\mathrm{H}_2$ may be replaced by hydrogen, as is the case in methylic alcohol. In the formulæ of the secondary and tertiary alcohols n may also $= 0$, but m must always be a positive integer.

NORMAL MONOHYDRIC ALCOHOLS.

General formula $\left\{\begin{array}{l}\mathbf{C}(\mathrm{C}_n\mathrm{H}_{2n+1})\mathrm{H}_2\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$.

The following is a list of the members of this class :—

		Fusing-points.	Boiling-points.
Methylic alcohol	$\left\{\begin{array}{l}\mathrm{H}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$	—	66·5°
Ethylic alcohol	$\left\{\begin{array}{l}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$	—	78·4
Propylic or tritylic alcohol	$\left\{\begin{array}{l}\mathbf{C}\mathrm{MeH_2}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}(\mathrm{CH_3})\mathrm{H_2}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$	—	97·4
Butylic or tetrylic alcohol	$\left\{\begin{array}{l}\mathbf{C}\mathrm{EtH_2}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}(\mathrm{C_2H_5})\mathrm{H_2}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$	—	116·9
Isobutylic alcohol	$\left\{\begin{array}{l}\mathbf{C}\mathrm{Me_2H}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}(\mathrm{CH_3})_2\mathrm{H}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$	—	109
Amylic or pentylic alcohol	$\left\{\begin{array}{l}\mathbf{C}\mathrm{PrH_2}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}(\mathrm{C_3H_7})\mathrm{H_2}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$	—	137
Isamylic alcohol......	$\left\{\begin{array}{l}\mathbf{C}\mathrm{Pr}\beta\mathrm{H_2}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}(\mathrm{CMe_2H})\mathrm{H_2}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$	−20°	129
Pseudamylic alcohol ..	$\left\{\begin{array}{l}\mathbf{C}\mathrm{EtMeH}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}(\mathrm{C_2H_5})(\mathrm{CH_3})\mathrm{H}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$	—	128
Caproylic or hexylic alcohol........	$\left\{\begin{array}{l}\mathbf{C}_5\mathrm{H}_{11}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$	—	157—158

		Fusing-points.	Boiling-points.
Œnanthylic or heptylic alcohol	$\left\{\begin{array}{l}C_6H_{13}\\CH_2Ho\end{array}\right.$	—	175°
Caprylic or octylic alcohol	$\left\{\begin{array}{l}C_7H_{15}\\CH_2Ho\end{array}\right.$	—	190—192
Nonylic alcohol	$\left\{\begin{array}{l}C_8H_{17}\\CH_2Ho\end{array}\right.$	—	200
Decatylic alcohol	$\left\{\begin{array}{l}C_9H_{19}\\CH_2Ho\end{array}\right.$	—	212
Cetylic alcohol	$\left\{\begin{array}{l}C_{15}H_{31}\\CH_2Ho\end{array}\right.$	50°	—
Cerotic alcohol	$\left\{\begin{array}{l}C_{26}H_{53}\\CH_2Ho\end{array}\right.$	79	—
Melissic alcohol	$\left\{\begin{array}{l}C_{29}H_{59}\\CH_2Ho\end{array}\right.$	85	—

The lower members of the class are liquid, and the higher solid. They are produced in a variety of operations, such as destructive distillation, fermentation, and animal secretion, but by reactions which cannot usually be traced.

Relations of the normal $C_nH_{2n+1}Ho$ *alcohols to the monad* C_nH_{2n+1} *radicals.*

1. The radicals C_nH_{2n+1} which are combined with hydroxyl in the normal alcohols may be separated, by first converting the alcohol into an iodide (see p. 128), and subsequently acting on the iodide by zinc (see p. 11).

2. The radical next lower in the series than that contained in the alcohol, may be obtained by converting the alcohol into the corresponding fatty acid, and then submitting a salt of this acid to electrolysis (see p. 12).

3. Inversely, the normal alcohols may be obtained by acting upon the normal radicals with chlorine under the influence of light, when one atom of hydrogen in the radical is displaced by chlorine.

Thus in the case of methyl we have

$$\underset{\text{Methyl.}}{\left\{\begin{array}{l}CH_3\\CH_3\end{array}\right.} + Cl_2 = \underset{\text{Chlorinated methyl.}}{\left\{\begin{array}{l}CH_3\\CH_2Cl\end{array}\right.} + \underset{\text{Hydrochloride acid.}}{HCl}:$$

by the action of potassic hydrate upon this chlorinated methyl, ethylic alcohol is formed, thus:—

$$\underset{\text{Chlorinated methyl.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2Cl\end{array}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Ethylic alcohol.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{array}\right.} + \underset{\text{Potassic chloride.}}{KCl.}$$

Relations of the normal $C_nH_{2n+1}Ho$ *alcohols to the dyad* C_nH_{2n} *radicals.*

1. The C_nH_{2n} radicals are obtained from the normal $C_nH_{2n+1}Ho$ alcohols by the abstraction of the elements of water:—

$$\underset{\text{Ethylic alcoholic.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{array}\right.} - \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Ethylene.}}{''\left\{\begin{array}{l}\mathbf{C}H_2\\ \mathbf{C}H_2\end{array}\right.}\cdot$$

2. Inversely, the normal alcohols are obtained from these radicals by first uniting the latter with hydrochloric, hydrobromic, or hydriodic acid, and then treating the product with potassic hydrate:—

$$\underset{\text{Ethylene.}}{''\left\{\begin{array}{l}\mathbf{C}H_2\\ \mathbf{C}H_2\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ethylic chloride.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2Cl\end{array}\right.}\cdot$$

$$\underset{\text{Ethylic chloride.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2Cl\end{array}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Ethylic alcohol.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{array}\right.} + \underset{\text{Potassic chloride.}}{KCl.}$$

or by uniting the dyad radicals with sulphuric acid, and distilling the product with water:—

$$\underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} + \underset{\text{Ethylene.}}{\mathbf{C}_2H_4} = \underset{\text{Sulphovinic acid.}}{\mathbf{S}O_2Ho(C_2H_5O):}$$

$$\underset{\text{Sulphovinic acid.}}{\mathbf{S}O_2EtoHo} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} + \underset{\text{Ethylic alcohol.}}{EtHo.}$$

Relations of the normal $C_nH_{2n+1}Ho$ *alcohols to the hydrides of the* C_nH_{2n+1} *radicals.*

1. When the alcohols are converted into iodides (see p. 128) and the latter digested with zinc and water at 100°, the corresponding hydrides are produced :—

$$\underset{\text{Zinc compound of radical.}}{Zn(C_nH_{2n+1})_2} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Zincic hydrate.}}{ZnHo_2} + \underset{\text{Hydride of radical.}}{2\left\{\begin{matrix}C_nH_{2n+1}\\ H\end{matrix}\right.}.$$

2. When the hydrides of the C_nH_{2n+1} radicals are acted upon by chlorine under the influence of light, they produce the chlorides of the radicals, from which the alcohols may be obtained by the action of potassic hydrate :—

$$\underset{\text{Ethylic hydride.}}{EtH} + Cl_2 = \underset{\text{Ethylic chloride.}}{EtCl} + \underset{\text{Hydrochloric acid.}}{HCl};$$

$$\underset{\text{Ethylic chloride.}}{EtCl} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Ethylic alcohol.}}{EtHo} + \underset{\text{Potassic chloride.}}{KCl}.$$

Relations of the $C_nH_{2n+1}Ho$ *alcohols to the radical cyanogen. Ascent of the alcohol series. Mendius's reaction.*

By the dry distillation of potassic sulphovinate and its homologues with potassic cyanide, the nitriles or abnormal cyanides of the radicals are produced :—

$$\underset{\text{Potassic sulphovinate.}}{SO_2EtoKo} + \underset{\text{Potassic cyanide.}}{KCy} = \underset{\text{Potassic sulphate.}}{SO_2Ko_2} + \underset{\text{Propionitrile.}}{EtCy}.$$

By treatment with nascent hydrogen, this ethylic nitrile is converted into propylamine :—

$$\underset{\text{Propionitrile.}}{N[C(CMeH_2)]'''} + 2H_2 = \underset{\text{Propylamine.}}{N[C(CMeH_2)H_2]H_2 \text{ or } NPrH_2}.$$

By the action of nitrous anhydride, propylamine is transformed into propylic alcohol:—

$$\underset{\text{Propylamine.}}{2NPrH_2} + \underset{\text{Nitrous anhydride.}}{N_2O_3} = \underset{\text{Propylic alcohol.}}{2PrHo} + \underset{\text{Water.}}{OH_2} + 2N_2.$$

It is obvious that by repeating these reactions on propylic alcohol, butylic alcohol would be obtained, the homologous series of alcohols being ascended one step at each repetition of the process. But in these reactions a secondary alcohol is generally formed at the same time.

METHYLIC ALCOHOL, *Carbinol, Wood Spirit, Pyroxylic Spirit.*

CH_3Ho or $MeHo$.

Molecular weight = 32. *Molecular volume* □□. 1 *litre of methylic alcohol vapour weighs* 16 *criths. Sp. gr.* 0·798. *Boils at* 66°·5.

Preparation.—1. From marsh-gas by the action of chlorine and subsequent treatment with potassic hydrate:—

$$\underset{\text{Marsh-gas.}}{CH_4} + Cl_2 = \underset{\text{Methylic chloride.}}{CH_3Cl} + \underset{\text{Hydrochloric acid.}}{HCl};$$

$$\underset{\text{Methylic chloride.}}{CH_3Cl} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Methylic alcohol.}}{CH_3Ho} + \underset{\text{Potassic chloride.}}{KCl}.$$

2. From the essential oil of *Gaultheria procumbens*, by the action of potassic hydrate:—

$$\underset{\text{Oil of \textit{Gaultheria procumbens}. (Methylic salicylate.)}}{C_7H_4OHoMeo} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Potassic salicylate.}}{C_7H_4OHoKo} + \underset{\text{Methylic alcohol.}}{MeHo}.$$

3. By the destructive distillation of wood.

Reactions.—1. Methylic alcohol unites with some salts in the capacity of water of crystallization, as, for instance:—

$$CaCl_2, 2MeHo.$$

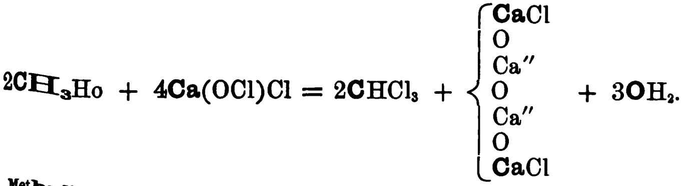
2. By the action of potassium and sodium, methylates are formed with elimination of hydrogen:—

$$\underset{\text{Potassic methylate.}}{CH_3Ko} \qquad \underset{\text{Sodic methylate.}}{CH_3Nao.}$$

3. By oxidation it is transformed into formic acid:—

$$\underset{\text{Methylic alcohol.}}{\left\{\begin{matrix} H \\ CH_2Ho \end{matrix}\right.} + O_2 = \underset{\text{Formic acid.}}{\left\{\begin{matrix} H \\ COHo \end{matrix}\right.} + \underset{\text{Water.}}{OH_2.}$$

4. When distilled with calcic chloro-hypochlorite (*chloride of lime*) and water, chloroform is produced:—



$$\underset{\text{Methylic alcohol.}}{2CH_3Ho} + \underset{\text{Calcic chloro-hypochlorite.}}{4Ca(OCl)Cl} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\text{Calcic oxychloride.}}{\left\{\begin{matrix} CaCl \\ O \\ Ca'' \\ O \\ Ca'' \\ O \\ CaCl \end{matrix}\right.} + \underset{\text{Water.}}{3OH_2.}$$

ETHYLIC ALCOHOL, *Alcohol, Spirit of Wine.*

$$\left\{\begin{matrix} CH_3 \\ CH_2Ho \end{matrix}\right. \text{ or } EtHo.$$

Molecular weight = 46. *Molecular volume* ☐☐. 1 *litre of ethylic alcohol vapour weighs* 23 *criths. Sp. gr.* 0·792 *at* 20°. *Boils at* 78°·4.

Preparation.—1. From ethylene (p. 80).

2. By the fermentation of grape-sugar with yeast at a temperature of about 22°:—

$$\underset{\text{Grape-sugar.}}{C_6H_{12}O_6} = \underset{\text{Ethylic alcohol.}}{2C_2H_5Ho} + \underset{\text{Carbonic anhydride.}}{2CO_2.}$$

At the same time, however, other products are formed, but in very small quantities.

Reactions.—1. Treated with potassium or sodium, alcohol forms ethylates :—

$$\underset{\text{Potassic ethylate.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2Ko^{\cdot}\end{matrix}\right.} \qquad \underset{\text{Sodic ethylate.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2Nao^{\cdot}\end{matrix}\right.}$$

2. Passed through a red-hot tube, alcohol is decomposed into marsh-gas, hydrogen, and carbonic oxide :—

$$\underset{\text{Ethylic alcohol.}}{\mathbf{C}_2H_5Ho} = \underset{\text{Marsh-gas.}}{\mathbf{C}H_4} + H_2 + \underset{\text{Carbonic oxide.}}{\mathbf{C}O.}$$

Small quantities of ethylene, benzene, and naphthalene are simultaneously produced, whilst carbon is deposited.

3. By oxidation, ethylic alcohol is converted first into aldehyde, and then into acetic acid :—

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{matrix}\right.} + O = \underset{\text{Aldehyde.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OH\end{matrix}\right.} + \underset{\text{Water.}}{OH_2.}$$

$$\underset{\text{Aldehyde.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OH\end{matrix}\right.} + O = \underset{\text{Acetic acid.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo^{\cdot}\end{matrix}\right.}$$

4. Distilled with chloride of lime, ethylic alcohol produces chloroform.

Alcoholates are salts containing alcohol in the place of water of crystallization; they are mostly decomposed immediately by water.

The following are known :—

$\mathbf{Zn}Cl_2, 2\mathbf{C}_2H_5Ho.$
$\mathbf{Ca}Cl_2, 4\mathbf{C}_2H_5Ho.$
$\mathbf{N}_2O_4Mgo'', 6\mathbf{C}_2H_5Ho.$

5. Treated with chlorine as long as hydrochloric acid is evolved, it is transformed into ethylic chloride and chloral hydrate (the hydrated aldehyde of trichloracetic acid :—

$$2\underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{matrix}\right.} + 4Cl_2 = \underset{\text{Chloral hydrate.}}{\left\{\begin{matrix}\mathbf{C}Cl_3\\ \mathbf{C}HHo_2\end{matrix}\right.} + \underset{\text{Ethylic chloride.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2Cl\end{matrix}\right.} + 4HCl.$$

MERCAPTAN, *Sulphur Alcohol, Ethylic Sulphhydrate, Hydrosulphate of Ethyl.*

$$\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_2Hs}\end{matrix}\right. \text{ or } \mathrm{EtHs}.$$

Molecular weight = 62. *Molecular volume* □□. 1 *litre of mercaptan vapour weighs* 31 *criths. Sp. gr. of liquid* 0·835. *Boils at* 36°.

Preparation.—By distilling potassic sulphovinate with potassic sulphhydrate :—

$$\begin{array}{ccccccc}\mathrm{SO_2EtoKo} & + & \mathrm{KHs} & = & \mathrm{EtHs} & + & \mathrm{SO_2Ko_2}.\\ \text{Potassic sulphovinate.} & & \text{Potassic sulphhydrate.} & & \text{Mercaptan.} & & \text{Potassic sulphate.}\end{array}$$

Reactions.—1. By the action of potassium and sodium on mercaptan, an atom of hydrogen is displaced by the metal, producing mercaptides :—

$$\begin{array}{cc}\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_2Ks}\end{matrix}\right. \cdot & \left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_2Nas}\end{matrix}\right. \cdot\\ \text{Potassic mercaptide.} & \text{Sodic mercaptide.}\end{array}$$

2. Mercaptan acts upon mercuric oxide with great energy, a white crystalline mercuric mercaptide being formed :—

$$\begin{array}{ccccccc}2\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_2Hs}\end{matrix}\right. & + & \mathrm{HgO} & = & \begin{matrix}\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_2}\end{matrix}\right.\\ \left\{\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_3}\end{matrix}\right.\end{matrix}\mathrm{Hgs''} & + & \mathrm{OH_2}.\\ \text{Mercaptan.} & & \text{Mercuric oxide.} & & \text{Mercuric mercaptide.} & & \text{Water.}\end{array}$$

Propylic alcohol, $\left\{\begin{matrix}\mathrm{CMeH_2}\\ \mathrm{CH_2Ho}\end{matrix}\right.$, is obtained from the fusel oil of the marc brandy of the south of France.

Isobutylic alcohol, $\left\{\begin{matrix}\mathrm{CMe_2H}\\ \mathrm{CH_2Ho}\end{matrix}\right.$, is contained in the fusel oil produced in the preparation of spirit from the molasses of beet-root sugar. Butylic alcohol of the formula $\left\{\begin{matrix}\mathrm{CEtH_2}\\ \mathrm{CH_2Ho}\end{matrix}\right.$ is obtained from butyric acid by Piria and Wurtz's reactions, described at p. 156.

Isamylic alcohol, $\left\{\begin{matrix}\mathrm{CPr\beta H_2}\\\mathrm{CH_2Ho}\end{matrix}\right.$, is the chief constituent of the fusel oil obtained in the manufacture of alcohol from potatoes or grain. Two other normal isomeric amylic alcohols are given in the Table at p. 78.

As far as these alcohols have been studied, they resemble, in their chemical relations, the two previously described.

SECONDARY MONOHYDRIC ALCOHOLS.

General formula.. $\left\{\begin{matrix}\mathrm{C(C_nH_{2n+1})H_2}\\\mathrm{C(C_mH_{2m+1})HHo}\end{matrix}\right.$.

The secondary alcohols differ from the normal in yielding, by oxidation, ketones instead of acids.

The following secondary alcohols are at present known:—

		Boiling-point.
Isopropylic alcohol or dimethyl carbinol	$\left\{\begin{matrix}\mathrm{CH_3}\\\mathrm{CMeHHo}\end{matrix}\right.$	82·8°
Methylethyl carbinol	$\left\{\begin{matrix}\mathrm{CH_3}\\\mathrm{CEtHHo}\end{matrix}\right.$	97
Diethyl carbinol	$\left\{\begin{matrix}\mathrm{CMeH_2}\\\mathrm{CEtHHo}\end{matrix}\right.$	116—117
Methylpropyl carbinol	$\left\{\begin{matrix}\mathrm{CH_3}\\\mathrm{CPrHHo}\end{matrix}\right.$	119
Methylisopropyl carbinol	$\left\{\begin{matrix}\mathrm{CMe_2H}\\\mathrm{CMeHHo}\end{matrix}\right.$	108
Pseudohexylic alcohol or methylbutyl carbinol	$\left\{\begin{matrix}\mathrm{CPrH_2}\\\mathrm{CMeHHo}\end{matrix}\right.$	137
Methyltertiarybutyl carbinol	$\left\{\begin{matrix}\mathrm{CMe_3}\\\mathrm{CMeHHo}\end{matrix}\right.$	120
Ethylpropyl carbinol	$\left\{\begin{matrix}\mathrm{CEtH_2}\\\mathrm{CEtHHo}\end{matrix}\right.$	135
Dipropyl carbinol	$\left\{\begin{matrix}\mathrm{CEtH_2}\\\mathrm{CPrHHo}\end{matrix}\right.$	150
Diisopropyl carbinol	$\left\{\begin{matrix}\mathrm{CMe_2H}\\\mathrm{C\beta PrHHo}\end{matrix}\right.$	131
Methylhexyl carbinol	$\left\{\begin{matrix}\mathrm{CH_3}\\\mathrm{C(C_6H_{13})HHo}\end{matrix}\right.$	179·5

		Boiling-point.
Methylnonyl carbinol ……	$\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{C(C_9H_{19})HHo}\end{matrix}\right.$ ..	229°

The first is obtained by the action of nascent hydrogen on acetone:—

$$\underset{\text{Acetone.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COMe}\end{matrix}\right.} + \mathrm{H_2} = \underset{\text{Isopropylic alcohol.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CMeHHo}\end{matrix}\right.}\cdot$$

The relation existing between ethylic alcohol, propylic alcohol, and isopropylic alcohol, will at once be evident from the following formulæ:—

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_2Ho}\cdot\end{matrix}\right.} \qquad \underset{\text{Propylic alcohol.}}{\left\{\begin{matrix}\mathrm{C(CH_3)H_2}\\ \mathrm{CH_2Ho}\ \cdot\end{matrix}\right.} \qquad \underset{\text{Isopropylic alcohol.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{C(CH_3)HHo}\cdot\end{matrix}\right.}$$

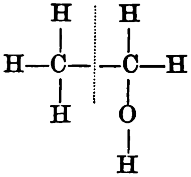
From these formulæ it is seen that propylic alcohol is ethylic alcohol, in which one atom of hydrogen in the methyl (or *non-oxygenated* part of the compound) is displaced by methyl; whereas isopropylic alcohol is ethylic alcohol in which one atom of hydrogen in the *oxygenated* part of the compound is displaced by methyl.

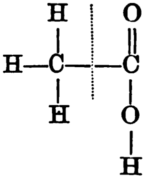
Ethylic alcohol boils at ..	78·4°
Propylic alcohol ,, ..	97·4
Isopropylic alcohol ,, ..	82·8

Thus, by substituting a semimolecule of methyl for one of hydrogen in the non-oxygenated part of the alcohol, the addition of CH_2 raises the boiling-point 19°; whilst, if an atom of hydrogen in the oxygenated part be similarly displaced, the same addition only raises the boiling point 4°·4.

Isopropylic alcohol yields by oxidation a ketone, and not an acid. The radical oxatyl being a necessary constituent in organic acids, it will be seen from the following equations that, although propylic alcohol can be converted into an acid without the disruption of its carbon atoms, isopropylic alcohol cannot be so transformed:—

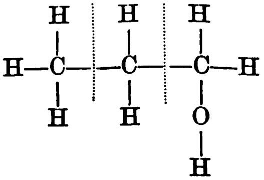
$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_2Ho}\end{matrix}\right.} + \mathrm{O_2} = \underset{\text{Acetic acid.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

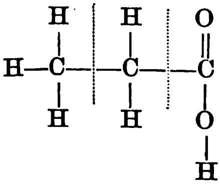




$$\left\{\begin{matrix}C(CH_3)H_2\\ CH_2Ho\end{matrix}\right. + O_2 = \left\{\begin{matrix}C(CH_3)H_2\\ COHo\end{matrix}\right. + OH_2.$$

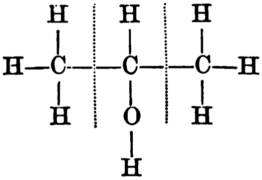
Propylic alcohol. Propionic acid. Water.

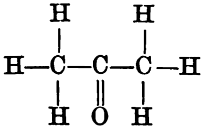




$$\left\{\begin{matrix}CH_3\\ C(CH_3)HHo\end{matrix}\right. + O = \left\{\begin{matrix}CH_3\\ CO(CH_3)\end{matrix}\right. + OH_2.$$

Isopropylic alcohol. Acetone. Water.





TERTIARY MONOHYDRIC ALCOHOLS.

General formula.. $\left\{\begin{matrix}C(C_nH_{2n+1})H_2\\ C(C_mH_{2m+1})_2Ho\end{matrix}\right.$

The following members of this series are known :—

		Boilin points
Pseudobutylic alcohol or trimethyl carbinol	CMe_3Ho	83—8
Dimethylethyl carbinol	$CEtMe_2Ho$	96—9
Dimethylpropyl carbinol....	$CPrMe_2Ho$	115

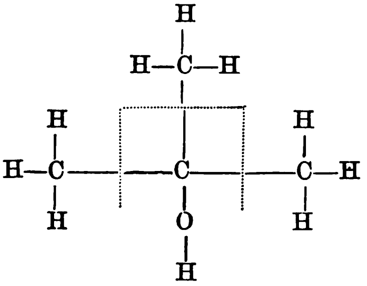
		Boiling points
Dimethylisopropyl carbinol	$C\beta PrMe_2Ho$	112°
Methyldiethyl carbinol	CEt_2MeHo	120
Triethyl carbinol	CEt_3Ho	141
Methylethylpropyl carbinol	$CPrEtMeHo$	135—138
Methylethylisopropyl carbinol	$C\beta PrEtMeHo$	124—127
Dimethylisobutyl carbinol ..	$C\beta BuMe_2Ho$	129—131
Dimethyltertiarybutyl carbinol	$\left\{\begin{matrix} CMe_3 \\ CMe_2Ho \end{matrix}\right.$	131—132
Diethylpropyl carbinol	$CPrEt_2Ho$	145—155

Pseudobutylic alcohol, $\left\{\begin{matrix} CH_3 \\ CMe_2Ho \end{matrix}\right.$, exists in small quantities in butylic alcohol obtained by fermentation; it has also been produced by acting with zincic methide on acetylic chloride, and submitting the product thus obtained to the action of water:—

$$\underset{\text{Acetylic chloride.}}{\left\{\begin{matrix} CH_3 \\ COCl \end{matrix}\right.} + \underset{\text{Zincic methide.}}{2ZnMe_2} = \left\{\begin{matrix} CH_3 \\ CMe_2(Zn''MeO) \end{matrix}\right. + \underset{\text{Zincic chlormethide.}}{ZnMeCl};$$

$$\left\{\begin{matrix} CH_3 \\ CMe_2(Zn''MeO) \end{matrix}\right. + \underset{\text{Water.}}{2OH_2} + \underset{\text{Pseudobutylic alcohol.}}{\left\{\begin{matrix} CH_3 \\ CMe_2Ho \end{matrix}\right.}$$

$$+ \underset{\text{Methylic hydride.}}{CH_4} + \underset{\text{Zincic hydrate.}}{ZnHo_2}.$$



or $\left\{\begin{matrix} CH_3 \\ C(CH_3)_2Ho \end{matrix}\right.$.

Pseudobutylic alcohol.

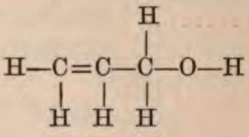
CHAPTER VII.

MONOHYDRIC ALCOHOLS:

Allyl or $C_nH_{2n-1}Ho$ series.

Only one alcohol of this series is known; it is a norm alcohol:—

$$\text{Allylic alcohol} \;\; .. \left\{ \begin{matrix} \mathbf{C}Me''H \\ \mathbf{C}H_2Ho \end{matrix} \right. .$$



$$\begin{matrix} & & & & & H & & & \\ & & & & & | & & & \\ H- & C & = & C & - & C & -O- & H \\ & | & & | & & | & & & \\ & H & & H & & H & & & \end{matrix}$$

Allylic alcohol.

ALLYLIC ALCOHOL.

$$\left\{ \begin{matrix} \mathbf{C}Me''H \\ \mathbf{C}H_2Ho \end{matrix} \right. \text{ or AllHo.}$$

Boils at 96°·5. *Sp. gr. of liquid at* 0° = 0·8709.

Preparation.—Glycerin, when submitted to the action diphosphorous tetriodide, yields allylic iodide:—

$$\underset{\substack{\text{Diphosphorous}\\\text{tetriodide.}}}{'\mathbf{P}''_2I_4} \;+\; \underset{\text{Glycerin.}}{2\left\{ \begin{matrix} \mathbf{C}H_2Ho \\ \mathbf{C}HHo \\ \mathbf{C}H_2Ho \end{matrix} \right.} \;=\; \underset{\substack{\text{Allylic}\\\text{iodide.}}}{2\;{}''\left\{ \begin{matrix} \mathbf{C}H_2 \\ \mathbf{C}H \\ \mathbf{C}H_2I \end{matrix} \right.} \;+\; \underset{\substack{\text{Phosphorous}\\\text{acid.}}}{2\mathbf{P}OHHo_2} \;+$$

The allylic iodide is then decomposed by argentic oxala when allylic oxalate is formed:—

$$\underset{\substack{\text{Allylic}\\\text{iodide.}}}{2AllI} \;+\; \underset{\substack{\text{Argentic}\\\text{oxalate.}}}{\left\{ \begin{matrix} \mathbf{C}OAgo \\ \mathbf{C}OAgo \end{matrix} \right.} \;=\; \underset{\substack{\text{Allylic}\\\text{oxalate.}}}{\left\{ \begin{matrix} \mathbf{C}OAllo \\ \mathbf{C}OAllo \end{matrix} \right.} \;+\; \underset{\substack{\text{Argentic}\\\text{iodide.}}}{2AgI.}$$

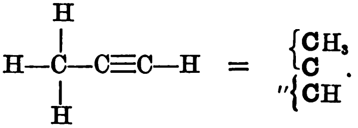
The allylic oxalate is next decomposed by ammonia, wh oxamide and allylic alcohol are produced:—

$$\underset{\substack{\text{Allylic}\\\text{oxalate.}}}{\left\{ \begin{matrix} \mathbf{C}OAllo \\ \mathbf{C}OAllo \end{matrix} \right.} \;+\; \underset{\text{Ammonia.}}{2\mathbf{N}H_3} \;=\; \underset{\text{Oxamide.}}{\left\{ \begin{matrix} \mathbf{C}O(\mathbf{N}'''H_2) \\ \mathbf{C}O(\mathbf{N}'''H_2) \end{matrix} \right.} \;+\; \underset{\substack{\text{Allylic}\\\text{alcohol.}}}{2AllH}$$

Reactions.—1. In all ordinary reactions, allylic alcohol behaves like ethylic alcohol. By oxidation it gives acrylic acid :—

$$\underset{\text{Allylic alcohol.}}{\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{CH_2Ho}\end{array}\right.} + \dot{\mathrm{O}}_2 = \underset{\text{Acrylic acid.}}{\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{COHo}\end{array}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

2. With phosphoric anhydride it yields allylene :—



$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C\equiv C-H}\\ & & | & & \\ & & \mathrm{H} & & \end{array} = \begin{array}{l}\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{C}\end{array}\right.\\ ''\{\mathrm{CH}\end{array}.$$

Among the ethereal salts of allylic alcohol, the sulphide and sulphocyanate occur in nature as garlic and mustard oils :—

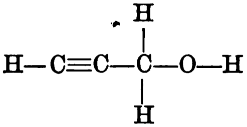
$$\underset{\substack{\text{Allylic sulphide.}\\ \text{(Garlic oil.)}}}{\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{CH_2}\\ \mathrm{S''}\\ \mathrm{CH_2}\\ \mathrm{CMe''H}\end{array}\right.} . \qquad \underset{\substack{\text{Allylic sulphocyanate.}\\ \text{(Mustard oil.)}}}{\begin{array}{l}\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{CH_2}\\ \mathrm{N}\end{array}\right.\\ ''\{\mathrm{CS''}\end{array}} .$$

MONOHYDRIC ALCOHOLS.

Propargyl or $C_nH_{2n-3}Ho$ series.

Only one alcohol of this series, a normal alcohol, is known :—

Propargylic alcohol $\begin{array}{l}'''\left\{\begin{array}{l}\mathrm{CH}\\ \mathrm{C}\end{array}\right.\\ \{\mathrm{CH_2Ho}\end{array}$.



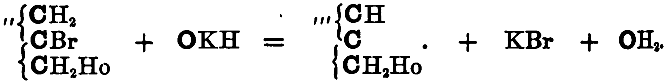
$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & | & & \\ \mathrm{H-C\equiv C} & - & \mathrm{C} & - & \mathrm{O-H}\\ & & | & & \\ & & \mathrm{H} & & \end{array}$$

PROPARGYLIC ALCOHOL.

$$\begin{array}{l}'''\left\{\begin{array}{l}\mathrm{CH}\\ \mathrm{C}\end{array}\right.\\ \{\mathrm{CH_2Ho}\end{array}.$$

Boils at 110—115°. *Sp. gr. of liquid at* 21° = 0·9628.

Preparation.—By the action of an aqueous solution of potassic hydrate on monobromallylic alcohol:—



$$''\left\{\begin{array}{l}CH_2\\CBr\\CH_2Ho\end{array}\right. + OKH = '''\left\{\begin{array}{l}CH\\C\\CH_2Ho\end{array}\right. . + KBr + OH_2.$$

Monobromallylic alcohol. Potassic hydrate. Propargylic alcohol. Potassic bromide. Water.

CHAPTER VIII.

MONOHYDRIC ALCOHOLS.

Phenyl or $C_nH_{2n-7}Ho$ series.

These alcohols may be divided into normal, secondary, and tertiary. The members of these three classes possess the general properties of the alcohols of the ethyl series. There is, however, in the phenyl series a class of alcohols in which the semimolecule of hydroxyl is directly united to the benzene nucleus. The members of this class are known as *phenols.* They may in one sense be regarded as a peculiar species of tertiary alcohols, inasmuch as the carbon atom to which the hydroxyl is united has its other bonds satisfied by carbon only. They exhibit a slightly acid character, dissolving in caustic alkalies, but being again expelled from this combination by carbonic anhydride.

CLASS I. *NORMAL ALCOHOLS.*

General formula $\left\{\begin{array}{l}C_nH_{2n-7}\\CH_2Ho\end{array}\right.$.

	Formula.	Fusing-point.	Boiling-point.
Benzylic alcohol........	$\left\{\begin{array}{l}C_6H_5\\CH_2Ho\end{array}\right.$	Liquid.	207°
Paratolylic alcohol......	$\left\{\begin{array}{l}C_6H_4Me\\CH_2Ho\end{array}\right.$ (1 : 4)	59°	217
Phenylethylic alcohol ..	$\left\{\begin{array}{l}CH_2(C_6H_5)\\CH_2Ho\end{array}\right.$	Liquid.	212

	Formula.	Fusing-point.	Boiling-point.
Phenylpropylic alcohol..	$\left\{\begin{array}{l}CH_2(CPhH_2)\\CH_2Ho\end{array}\right.$	Liquid.	235°
Cumylic alcohol........	$\left\{\begin{array}{l}C_6H_4\beta Pr\\CH_2Ho\end{array}\right.$ (1 : 4)	Liquid.	243
Sycocerylic alcohol......	$\left\{\begin{array}{l}C_{17}H_{27}\\CH_2Ho\end{array}\right.$	90°	—

Class II. *SECONDARY ALCOHOLS.*

a. General formula $\left\{\begin{array}{l}C_nH_{2n-7}\\C(C_nH_{2n+1})HHo\end{array}\right.$.

	Formula.	Fusing-point.	Boiling-point.
Phenylmethyl carbinol..	$\left\{\begin{array}{l}C_6H_5\\CMeHHo\end{array}\right.$	Liquid.	202—203°
Phenylethyl carbinol....	$\left\{\begin{array}{l}C_6H_5\\CEtHHo\end{array}\right.$	Liquid.	210—211

b. General formula $\left\{\begin{array}{l}C_nH_{2n-7}\\C(C_nH_{2n-7})HHo\end{array}\right.$.

	Formula.	Fusing-point.	Boiling-point.
Diphenyl carbinol......	$\left\{\begin{array}{l}C_6H_5\\C(C_6H_5)HHo\end{array}\right.$	67·5—68°	297—298°
Benzylphenyl carbinol ..	$\left\{\begin{array}{l}C(C_6H_5)H_2\\C(C_6H_5)HHo\end{array}\right.$	62	—
Ditolyl carbinol........	$\left\{\begin{array}{l}C_6H_4Me\\C(C_6H_4Me)HHo\end{array}\right.$	69	—

Class III. *TERTIARY ALCOHOLS.*

a. General formula $\left\{\begin{array}{l}C_nH_{2n-7}\\C(C_nH_{2n+1})_2Ho\end{array}\right.$.

	Formula.	Fusing-point.	Boiling-point.
Benzyldimethyl carbinol	$\left\{\begin{array}{l}C(C_6H_5)H_2\\CMe_2Ho\end{array}\right.$	20—22°	220—230°.

b. General formula $\left\{\begin{array}{l}C_nH_{2n-7}\\C(C_nH_{2n-7})(C_nH_{2n+1})Ho\end{array}\right.$.

No example of this subdivision has yet been prepared.

$$\therefore \text{ General formula } \left\{\begin{matrix} C_nH_{2n-7} \\ C(C_nH_{2n-7})_2Ho \end{matrix}\right.$$

	Formula.	Fusing-point.	Boiling-point.
Triphenyl carbinol	$\left\{\begin{matrix} C_6H_5 \\ CPh_2Ho \end{matrix}\right.$	157°	Above 360°—

CLASS IV. *PHENOLS.*

General formula $C_nH_{2n-7}Ho$.

	Formula.	Fusing-point.	Boiling-point.
Phenol (carbolic acid, phenylic alcohol) ..	C_6H_5Ho	42°	181·5°
Orthocresol..........	C_6H_4MeHo (1 : 2)	31—31·5	185—186
Metacresol	C_6H_4MeHo (1 : 3)	liquid	201
Paracresol	C_6H_4MeHo (1 : 4)	36	199
Xylenol (dimethylphenol, 5 isomers known)	$C_6H_3Me_2Ho$	—	—
Paraethylphenol	C_6H_4EtHo (1 : 4)	47	211
Phlorol	C_6H_4EtHo	liquid	220
Mesitylol............	$C_6H_2Me_3Ho$ (1 : 3 : 5 : 6)	68—69	220
Pseudocumenol	$C_6H_2Me_3Ho$	69	240
Thymol	$C_6H_3\beta PrMeHo$ (1 : 4 : 6)	44	230
Carvacrol	$C_6H_3\beta PrMeHo$ (1 : 4 : 5)	liquid	233—235

A dihydric compound which combines the properties of a phenol and a normal alcohol, is saligenin, $\left\{\begin{matrix} C_6H_4Ho \\ CH_2Ho \end{matrix}\right.$ (1 : 2), the alcohol corresponding to salicylic acid.

CLASS I. *NORMAL ALCOHOLS.*

BENZYLIC ALCOHOL.

$$\left\{\begin{matrix} C_6H_5 \\ CH_2Ho \end{matrix}\right.$$

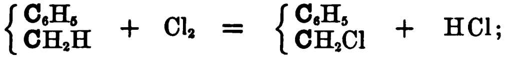
Boils at 207°. *Sp. gr. of liquid* 1·06.

Preparation.—1. By treating oil of bitter almonds with alcoholic potash:—

$$2\left\{\begin{matrix} C_6H_5 \\ COH \end{matrix}\right. + KHo + \left\{\begin{matrix} C_6H_5 \\ CH_2Ho \end{matrix}\right. + \left\{\begin{matrix} C_6H_5 \\ COKo \end{matrix}\right. .$$

Benzoic aldehyde. (Oil of bitter almonds.)	Potassic hydrate.	Benzylic alcohol.	Potassic benzoate.

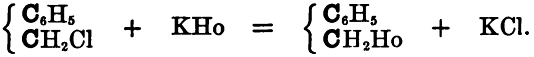
2. Benzylic alcohol may be obtained from toluol by first converting the latter into benzylic chloride by the action of chlorine—



$$\left\{\begin{matrix}C_6H_5\\CH_2H\end{matrix}\right. + Cl_2 = \left\{\begin{matrix}C_6H_5\\CH_2Cl\end{matrix}\right. + HCl;$$

Toluol. (Benzylic hydride.)
Benzylic chloride.
Hydrochloric acid.

and then submitting the benzylic chloride to the action of potassic hydrate:—



$$\left\{\begin{matrix}C_6H_5\\CH_2Cl\end{matrix}\right. + KHo = \left\{\begin{matrix}C_6H_5\\CH_2Ho\end{matrix}\right. + KCl.$$

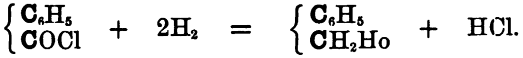
Benzylic chloride.
Potassic hydrate.
Benzylic alcohol.
Potassic chloride.

3. By digesting benzylic chloride with freshly precipitated plumbic hydrate:—

$$2\left\{\begin{matrix}C_6H_5\\CH_2Cl\end{matrix}\right. + PbHo_2 = PbCl_2 + 2\left\{\begin{matrix}C_6H_5\\CH_2Ho.\end{matrix}\right.$$

Benzylic chloride.
Plumbic hydrate.
Plumbic chloride.
Benzylic alcohol.

4. By passing a mixture of hydrogen and the vapour of benzoylic chloride over heated spongy palladium:—

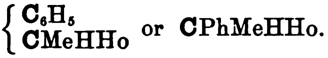


$$\left\{\begin{matrix}C_6H_5\\COCl\end{matrix}\right. + 2H_2 = \left\{\begin{matrix}C_6H_5\\CH_2Ho\end{matrix}\right. + HCl.$$

Benzoylic chloride.
Benzylic alcohol.

CLASS II. *SECONDARY ALCOHOLS.*

PHENYLMETHYL CARBINOL.



$$\left\{\begin{matrix}C_6H_5\\CMeHHo\end{matrix}\right. \text{ or } CPhMeHHo.$$

Sp. gr. of liquid at 0° = 1·013. *Boils at* 202—203°.

Preparation.—By the action of sodium amalgam on an aqueous-alcoholic solution of methylphenylketone (acetophenone):—

$$COPhMe + H_2 = CPhMeHHo.$$

Acetophenone.
Phenylmethyl carbinol.

CLASS III. *TERTIARY ALCOHOLS.*

TRIPHENYL CARBINOL.

CPh_3Ho.

Fuses at 157°. *Boils above* 360°.

Preparation.—By treating a mixture of equal molecules of diphenylcarbinol and benzene with dehydrating agents, triphenylmethylic hydride is obtained:—

$$\underset{\text{Diphenyl carbinol.}}{CPh_2HHo} + \underset{\text{Benzene.}}{PhH} = \underset{\text{Triphenylmethylic hydride.}}{CPh_3H} + \underset{\text{Water.}}{OH_2}.$$

When this compound is oxidized with chromic acid, it is converted into triphenyl carbinol:—

$$\underset{\text{Triphenylmethylic hydride.}}{2CPh_3H} + O_2 = \underset{\text{Triphenyl carbinol.}}{2CPh_3Ho}.$$

CLASS IV. *PHENOLS.*

PHENOL, *Phenylic Alcohol, Carbolic Acid, Phenylic Acid.*

C_6H_5Ho or $PhHo$.

Molecular weight = 94. *Molecular volume* ☐☐. 1 *litre of phenol vapour weighs* 47 *criths. Sp. gr.* 1·065 *at* 18°. *Fuses at* 42°. *Boils at* 181°·5.

Occurrence.—In coal-tar, and in small quantity in the urine of man, of the cow, and of the horse.

Preparation.—1. By the distillation of salicylic acid with baryta or lime:—

$$\underset{\text{Salicylic acid.}}{\left\{\begin{matrix} C_6H_4Ho \\ COHo \end{matrix}\right.} = \underset{\text{Phenol.}}{C_6H_5Ho} + \underset{\text{Carbonic anhydride.}}{CO_2}.$$

2. By fusing potassic benzenesulphonate with potassic hydrate:—

$$\underset{\text{Potassic benzenesulphonate.}}{\left\{\begin{matrix} C_6H_5 \\ SO_2Ko \end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Phenol.}}{C_6H_5Ho} + \underset{\text{Potassic sulphite.}}{SOKo_2}.$$

3. By boiling diazobenzene nitrate with water (see p. 69).

4. It is also produced in the destructive distillation of numerous organic substances.

5. Phenol is formed when the vapour of ethylic alcohol or acetic acid is passed through a red-hot tube. In this manner phenylic compounds may be obtained from their elements; for both acetic acid and alcohol may be built up from carbon, hydrogen, and oxygen.

Reactions.—Treated with chlorine, bromine, or nitric acid, phenol produces a series of substitution products, of which the following are examples :—

Dichlorphenol	$C_6H_3Cl_2Ho$.
Trichlorphenol..............	$C_6H_2Cl_3Ho$.
Perchlorphenol..............	C_6Cl_5Ho.
Bromphenol	C_6H_4BrHo.
Nitrophenol	$C_6H_4(N^vO_2)Ho$.
Dinitrophenol	$C_6H_3(N^vO_2)_2Ho$.
Trinitrophenol (*Picric acid*) ...	$C_6H_2(N^vO_2)_3Ho$.
Amidodinitrophenol (*Picramic acid*)	$C_6H_2(N'''H_2)(N^vO_2)_2Ho$.

CHAPTER IX.

DIHYDRIC ALCOHOLS.

Glycol or $C_nH_{2n}Ho_2$ series.

The following is a list of the glycols at present known, with their constitutional formulæ :—

		Boiling-point.
Glycol or Ethylic glycol...	$\left\{\begin{array}{l}CH_2Ho\\CH_2Ho\end{array}\right.$	197·5°
Propylic glycol (*a*)	$\left\{\begin{array}{l}CH_2Ho\\CH_2\\CH_2Ho\end{array}\right.$	216
" " (*b*)	$\left\{\begin{array}{l}CMeHHo\\CH_2Ho\end{array}\right.$	188—189

			Boiling-p
Butylic glycol (*a*)	$\left\{\begin{matrix}\mathbf{C}MeHHo\\ \mathbf{C}H_2\\ \mathbf{C}H_2Ho\end{matrix}\right.$		203·5—2
” ” (*b*)	$\left\{\begin{matrix}\mathbf{C}EtHHo\\ \mathbf{C}H_2Ho\end{matrix}\right.$		191—1
” ” (*c*)	$\left\{\begin{matrix}\mathbf{C}MeHHo\\ \mathbf{C}MeHHo\end{matrix}\right.$		183—1
” ” (*d*)	$\left\{\begin{matrix}\mathbf{C}Me_2Ho\\ \mathbf{C}H_2Ho\end{matrix}\right.$		176—1
Amylic glycol (*a*)	$\left\{\begin{matrix}\mathbf{C}EtHHo\\ \mathbf{C}MeHHo\end{matrix}\right.$		187·
” ” (*b*)	$\left\{\begin{matrix}\mathbf{C}\beta PrHHo\\ \mathbf{C}H_2Ho\end{matrix}\right.$		206
” ” (*c*)	$\left\{\begin{matrix}\mathbf{C}Me_2Ho\\ \mathbf{C}MeHHo\end{matrix}\right.$		177
Hexylic glycol (*a*)	$\left\{\begin{matrix}\mathbf{C}BuHHo\\ \mathbf{C}H_2Ho\end{matrix}\right.$		207
” ” (*b*)	$\mathbf{C}_6H_{12}Ho_2$		212—2
” ” (*c*) (Pinakone)	$\left\{\begin{matrix}\mathbf{C}Me_2Ho\\ \mathbf{C}Me_2Ho\end{matrix}\right.$	(fuses at 35—38°)	171—1
Octylic glycol (*a*)	$\mathbf{C}_8H_{16}Ho_2$		235—2
” ” (*b*) ..... (Ethylmethylpinakone)	$\left\{\begin{matrix}\mathbf{C}EtMeHo\\ \mathbf{C}EtMeHo\end{matrix}\right.$	(fuses at 28°)	200—2

Methylic glycol has not been prepared, but its dimeth ether, $\mathbf{C}H_2Meo_2$, methylal, is known.

It will be observed that the boiling-points of the gly often differ from each other in a direction inverse to that viously noticed in the case of the normal monohydric alcol the more complex substances frequently boiling at a lo temperature than the simpler ones.

GLYCOL. ETHYLIC GLYCOL, *Ethylenic Alcohol.*

$$\left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Ho\end{matrix}\right. .$$

Molecular weight = 62. *Molecular volume* □□. 1 *litr ethylic glycol vapour weighs* 31 *criths. Sp. gr.* 1· *Boils at* 197°·5.

Preparation.—Ethylenic dibromide is treated with arge *acetate,* and thus converted into ethylenic diacetate:—

$$\underset{\text{Ethylenic dibromide.}}{\left\{\begin{array}{l}CH_2Br\\CH_2Br\end{array}\right.} + \underset{\text{Argentic acetate.}}{2CMeOAgo} = \underset{\substack{\text{Ethylenic diacetate.}\\\text{(Diacetic glycol.)}}}{\left\{\begin{array}{l}CH_2\text{-}O\text{-}CMeO\\CH_2\text{-}O\text{-}CMeO\end{array}\right.} + \underset{\substack{\text{Argentic}\\\text{bromide.}}}{2AgBr.}$$

The ethylenic diacetate is now acted upon by potassic hydrate, and yields potassic acetate and glycol:—

$$\underset{\text{Ethylene diacetate.}}{\left\{\begin{array}{l}CH_2\text{-}O\text{-}CMeO\\CH_2\text{-}O\text{-}CMeO\end{array}\right.} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{2KHo} = \underset{\text{Glycol.}}{\left\{\begin{array}{l}CH_2Ho\\CH_2Ho\end{array}\right.} + \underset{\text{Potassic acetate.}}{2CMeOKo.}$$

Reactions.—1. Glycol is easily oxidized, the first product of its oxidation being glycollic acid:—

$$\underset{\text{Glycol.}}{\left\{\begin{array}{l}CH_2Ho\\CH_2Ho\end{array}\right.} + O_2 = \underset{\substack{\text{Glycollic}\\\text{acid.}}}{\left\{\begin{array}{l}CH_2Ho\\COHo\end{array}\right.} + \underset{\text{Water.}}{OH_2.}$$

2. By further oxidation oxalic acid is formed:—

$$\underset{\text{Glycol.}}{\left\{\begin{array}{l}CH_2Ho\\CH_2Ho\end{array}\right.} + 2O_2 = \underset{\substack{\text{Oxalic}\\\text{acid.}}}{\left\{\begin{array}{l}COHo\\COHo\end{array}\right.} + \underset{\text{Water.}}{2OH_2.}$$

3. Potassic oxalate is produced by heating glycol and potassic hydrate together to 250°:—

$$\underset{\text{Glycol.}}{\left\{\begin{array}{l}CH_2Ho\\CH_2Ho\end{array}\right.} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{2KHo} = \underset{\substack{\text{Potassic}\\\text{oxalate.}}}{\left\{\begin{array}{l}COKo\\COKo\end{array}\right.} + 4H_2.$$

4. Treated with potassium or sodium, the hydrogen of the hydroxyl in glycol is replaced in two successive stages:—

$$\underset{\text{Monosodic glycol.}}{\left\{\begin{array}{l}CH_2Nao\\CH_2Ho\end{array}\right.;} \qquad \underset{\text{Disodic glycol.}}{\left\{\begin{array}{l}CH_2Nao\\CH_2Nao\end{array}\right..}$$

The following list contains some of the principal derivatives of glycol:—

$$\underset{\text{Glycol.}}{\left\{\begin{array}{l}CH_2Ho\\CH_2Ho\end{array}\right..} \qquad \underset{\text{Sulphur glycol.}}{\left\{\begin{array}{l}CH_2Hs\\CH_2Hs\end{array}\right..}$$

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$$\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Cl\end{array}\right. .$$

Chlorhydric glycol.

$$\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Br\end{array}\right. .$$

Bromhydric glycol.

$$\left\{\begin{array}{l}\mathbf{C}H_2Eto\\ \mathbf{C}H_2Br\end{array}\right. .$$

Bromethylic glycol.

$$\left\{\begin{array}{l}\mathbf{C}H_2Eto\\ \mathbf{C}H_2Ho\end{array}\right. .$$

Hydric ethylic glycol.

$$\left\{\begin{array}{l}\mathbf{C}H_2Eto\\ \mathbf{C}H_2Eto\end{array}\right. .$$

Diethylic glycol.

$$\left\{\begin{array}{l}\mathbf{C}H_2Br\\ \mathbf{C}H_2\\ O\\ \mathbf{C}O\\ \mathbf{C}H_3\end{array}\right. \text{ or } \left\{\begin{array}{l}\mathbf{C}H_2Br\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\end{array}\right. .$$

Glycollic acetobromide.

$$\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}H_2\\ O\\ \mathbf{C}O\\ \mathbf{C}H_3\end{array}\right. \text{ or } \left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\end{array}\right. .$$

Monacetic glycol.

$$\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}O\\ O\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ O\\ \mathbf{C}O\\ \mathbf{C}H_3\end{array}\right. \text{ or } \left\{\begin{array}{l}\mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\end{array}\right. .$$

Diacetic glycol.

$$\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}O\\ O\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ O\\ \mathbf{C}O\\ \mathbf{C}(C_2H_5)H_2\end{array}\right. \text{ or } \left\{\begin{array}{l}\mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}PrO\end{array}\right. .$$

Acetobutyric glycol.

POLYETHYLENIC GLYCOLS,

Polyethylenic Alcohols.

These bodies are produced by heating ethylenic oxide with glycol in sealed tubes, and by other processes. They may be regarded as formed by the addition of ethylenic oxide to *glycol*.

Diethylenic glycol...... $\left\{\begin{array}{l}CH_2Ho\\CH_2\\O\\CH_2\\CH_2Ho\end{array}\right.$.

Triethylenic glycol .... $\left\{\begin{array}{l}CH_2Ho\\CH_2\\O\\CH_2\\CH_2\\O\\CH_2\\CH_2Ho\end{array}\right.$.

Tetrethylenic glycol .... $\left\{\begin{array}{l}CH_2Ho\\CH_2\\O\\CH_2\\CH_2\\O\\CH_2\\CH_2\\O\\CH_2\\CH_2Ho\end{array}\right.$.

Pentethylenic and hexethylenic glycols have also been rmed.

CHAPTER X.

DIHYDRIC ALCOHOLS.

Orcin, or $C_nH_{2n-8}Ho_2$ series.

The orcin series of alcohols are derived from benzene and s homologues by the substitution of two semimolecules of ydroxyl for two hydrogen atoms of the nucleus. They erefore belong to the class of the phenols or phenylic lcohols. The following members of this series are known:—

		Fusing-point.	Boiling-point.
Pyrocatechin (orthodioxybenzene) ..	$C_6H_4Ho_2$ (1 : 2)	104°	245°
Resorcin (metadioxybenzene)......	$C_6H_4Ho_2$ (1 : 3)	118	276
Hydroquinone (paradioxybenzene) .	$C_6H_4Ho_2$ (1 : 4)	172·5	—
Orcin	$C_6H_3MeHo_2$	86	290
Iso-orcin......................	$C_6H_3MeHo_2$ (1 : 2 : 4)	87	260
Homopyrocatechin	$C_6H_3MeHo_2$ (1 : 3 : 4)	semi-liquid	—
Hydrotoluquinone	$C_6H_3MeHo_2$ (1 : 2 : 5)	124°	—
Hydrophlorone..................	$C_8H_8Ho_2$	—	—

PYROCATECHIN.

$C_6H_4Ho_2$ (1 : 2).

Fuses at 104°. *Boils at* 245°.

Preparation.—1. By fusing potassic orthophenolsulphonate with potassic hydrate:—

$$\underset{\text{Potassic ortho-phenolsulphonate.}}{C_6H_4Ho(SO_2Ko)\,(1:2)} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Pyrocatechin.}}{C_6H_4Ho_2\,(1:2)} + \underset{\text{Potassic sulphite.}}{SOKo_2}.$$

2. By the dry distillation of catechu gum.

The monomethyl ether of pyrocatechin, C_6H_4MeoHo (1 : 2), occurs in beechwood creosote.

RESORCIN.

$C_6H_4Ho_2$ (1 : 3).

Fuses at 118°. *Boils at* 276°.

Preparation.—1. By fusing potassic metabenzenedisulphonate with potassic hydrate:—

$$\underset{\text{Potassic meta-benzene-disulphonate.}}{C_6H_4(SO_2Ko)_2\,(1:3)} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Resorcin.}}{C_6H_4Ho_2\,(1:3)} + \underset{\text{Potassic sulphite.}}{2SOKo_2}.$$

2. By fusing *Galbanum asafœtida* and various other resins with potassic hydrate.

HYDROQUINONE.

$C_6H_4Ho_2$ (1 : 4).

Preparation.—1. By treating arbutin with emulsin, or by boiling it with dilute sulphuric acid:—

$$C_{12}H_{16}O_7 + OH_2 = C_6H_4Ho_2 + C_6H_{12}O_6.$$

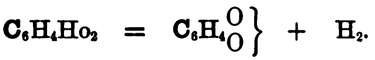
Arbutin. Hydroquinone. Glucose.

2. By the action of sulphurous acid upon a solution of quinone.

3. By the destructive distillation of quinic acid.

4. From para-amidophenol, $C_6H_4Ho(NH_2)$ (1:4) by treatment with nitrous anhydride and subsequent boiling with water (see diazo-reactions, p. 69).

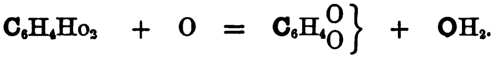
Reactions.—1. Passed in vapour through a red-hot tube, it is decomposed into quinone and hydrogen:—



$$C_6H_4Ho_2 = C_6H_4\left.\begin{matrix}O\\O\end{matrix}\right\} + H_2.$$

Hydroquinone. Quinone.

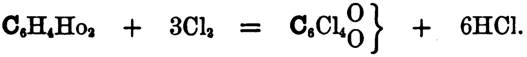
2. By many oxidizing agents it is transformed into quinone:—



$$C_6H_4Ho_2 + O = C_6H_4\left.\begin{matrix}O\\O\end{matrix}\right\} + OH_2.$$

Hydroquinone. Quinone.

3. By the action of chlorine or a mixture of potassic chlorate and hydrochloric acid, it is converted into perchloroquinone (chloranil):—



$$C_6H_4Ho_2 + 3Cl_2 = C_6Cl_4\left.\begin{matrix}O\\O\end{matrix}\right\} + 6HCl.$$

Hydroquinone. Chloranil.

ORCIN.

$C_6MeH_3Ho_2$.

Melts at 86°. *Boils at about* 290°.

Occurrence.—In certain lichens, such as *Lecanora tartarea*, *Roccella tinctoria*, and *Variolaria orcina.*

Preparation.—By the dry distillation of orsellinic acid, or by boiling this acid with powerful bases:—

$$C_8H_8O_4 = C_6MeH_3Ho_2 + CO_2.$$

Orsellinic acid. Orcin.

Many other bodies which are obtained from lichens, such as lecanoric acid, erythrin, and picroerythrin, yield orcin under similar treatment; but all these compounds give first orsellinic acid, which then breaks up into orcin and carbonic anhydride; thus:—

$$\underset{\text{Lecanoric acid.}}{C_{16}H_{14}O_7} + OH_2 = \underset{\text{Orsellinic acid.}}{2C_8H_8O_4}.$$

$$\underset{\text{Erythric acid.}}{C_{20}H_{22}O_{10}} + 2OH_2 = \underset{\text{Erythrite.}}{C_4H_{10}O_4} + \underset{\text{Orsellinic acid.}}{2C_8H_8O_4}.$$

$$\underset{\text{Picroerythrin.}}{C_{12}H_{16}O_7} + OH_2 = \underset{\text{Erythrite.}}{C_4H_{10}O_4} + \underset{\text{Orsellinic acid.}}{C_8H_8O_4}.$$

Reactions.—1. With chlorine, bromine, iodine, and nitric acid, orcin gives the following substitution products:—

		Melting-point.
Monobromorcin......	$C_6MeH_2BrHo_2$......	135°
Tribromorcin........	$C_6MeBr_3Ho_2$	103
Trichlororcin........	$C_6MeCl_3Ho_2$........	159
Triiodorcin..........	$CMeI_3Ho_2$	—
Trinitro-orcinic acid..	$C_6Me(NO_2)_3Ho_2$....	163

2. By treatment with ammonia in the presence of free oxygen it yields orcein, the colouring-matter of *Archil* and *Cudbear*, the reaction being probably the following:—

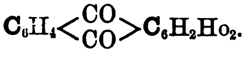
$$\underset{\text{Orcin.}}{C_6MeH_3Ho_2} + NH_3 + O_3 = \underset{\text{Orcein.}}{C_6MeH_3(N^vO_2)Ho}\,? + 2OH_2$$

The so-called *betaorcin* is the monomethyl ether of orcin, $C_6H_3MeMeoHo$.

ALIZARIN,

$$C_{14}H_6O_2Ho_2.$$

Alizarin, the chief colouring-matter of the madder root, is a dihydric phenol derived from anthraquinone $C(_{14}H_8O_2)$ (see p. 75). The formula of alizarin is—



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2Ho_2.$$

It may be prepared artificially in the following manner.

Anthraquinone, when heated with concentrated sulphuric acid, yields anthraquinone-sulphonic acid:—

$$\underset{\text{Anthraquinone.}}{C_{14}H_8O_2} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Anthraquinone-sulphonic acid.}}{C_{14}H_7O_2(SO_2Ho)} + \underset{\text{Water.}}{OH_2}.$$

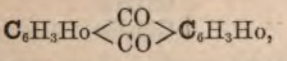
When the potash salt of anthraquinone-sulphonic acid is fused with caustic potash, the monad group (SO_2Ko) is replaced by potassoxyl, whilst at the same time a second semimolecule of potassoxyl is introduced, hydrogen being evolved. The product is potassic alizarate:—

$$\underset{\text{Potassic anthraquinone-sulphonate.}}{C_{14}H_7O_2(SO_2Ko)} + \underset{\text{Potassic hydrate.}}{3KHo} = \underset{\text{Potassic alizarate.}}{C_{14}H_6O_2Ko_2} + \underset{\text{Potassic sulphite.}}{SOKo_2}$$

$$+ \underset{\text{Water.}}{OH_2} + H_2.$$

On the addition of an acid to an aqueous solution of potassic alizarate, alizarin ($C_{14}H_6O_2Ho_2$) identical in properties with the natural product from the madder root, is precipitated.

Anthraflavin,



$$C_6H_3Ho{<}{\substack{CO\\CO}}{>}C_6H_3Ho,$$

isomeric with alizarin, but possessing no tinctorial properties, is usually simultaneously formed in the above reactions.

CHAPTER XI.

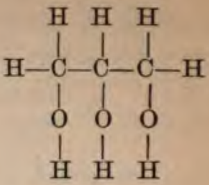
TRIHYDRIC ALCOHOLS.

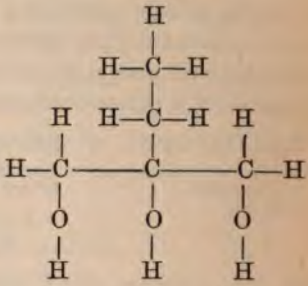
Glycerin or $C_nH_{2n-1}Ho_3$ series.

These alcohols contain three semimolecules of hydroxyl united with three different atoms of carbon; consequently the lowest term of the series contains three atoms of carbon.

Only two of these alcohols have been hitherto obtained:—

$$\text{Glycerin} \ldots\ldots \left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\ .\\ \mathbf{C}H_2Ho\end{array}\right.$$





$$\text{Amylglycerin} \ldots \left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}EtHo\ ?\\ \mathbf{C}H_2Ho\end{array}\right.$$

The constitution of amylglycerin is not at present established. Its formula may possibly be

$$\left\{\begin{array}{l}\mathbf{C}EtHHo\\ \mathbf{C}HHo\quad .\\ \mathbf{C}H_2Ho\end{array}\right.$$

The action of oxidizing agents on amylglycerin will probably throw light upon its internal structure.

GLYCERIN.

$$\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\ .\\ \mathbf{C}H_2Ho\end{array}\right.$$

Sp. gr. of liquid at 15°·4 *is* 1·26. *Crystallizes at low temperatures, and remains solid afterwards at ordinary temperatures. Boils in vacuo at* 179°·5.

Sources.—Most animal and vegetable fats consist of mixtures of the glycerin ethereal salts of the fatty, and of the oleic, series of acids. Glycerin is liberated from these by water at high temperatures, or by bases giving salts insoluble in water:—

$$\underset{\text{Stearin.}}{\left\{\begin{array}{l}\mathbf{CH}_2\text{-O-}\mathbf{C}(\mathrm{C}_{17}\mathrm{H}_{35})\mathrm{O}\\ \mathbf{CH}\text{ -O-}\mathbf{C}(\mathrm{C}_{17}\mathrm{H}_{35})\mathrm{O}\\ \mathbf{CH}_2\text{-O-}\mathbf{C}(\mathrm{C}_{17}\mathrm{H}_{35})\mathrm{O}\end{array}\right.} + \underset{\text{Water.}}{3\mathbf{O}\mathrm{H}_2} = \underset{\text{Glycerin.}}{\left\{\begin{array}{l}\mathbf{CH}_2\mathrm{Ho}\\ \mathbf{CH}\mathrm{Ho}\\ \mathbf{CH}_2\mathrm{Ho}\end{array}\right.} + 3\underset{\text{Stearic acid.}}{\left\{\begin{array}{l}\mathbf{C}_{17}\mathrm{H}_{35}\\ \mathbf{CO}\mathrm{Ho}\end{array}\right.}.$$

Relation of Glycerin to Isopropylic Alcohol.

By the action of hydriodic acid, glycerin is converted into isopropylic iodide:—

$$\underset{\text{Glycerin.}}{\left\{\begin{array}{l}\mathbf{CH}_2\mathrm{Ho}\\ \mathbf{CH}\mathrm{Ho}\\ \mathbf{CH}_2\mathrm{Ho}\end{array}\right.} + \underset{\text{Hydriodic acid.}}{5\mathrm{HI}} = \underset{\text{Isopropylic iodide.}}{\left\{\begin{array}{l}\mathbf{CH}_3\\ \mathbf{CH}\mathrm{I}\\ \mathbf{CH}_3\end{array}\right.} + 2\mathrm{I}_2 + \underset{\text{Water.}}{3\mathbf{O}\mathrm{H}_2}.$$

Relation of Glycerin to Allylic Alcohol.

When a diphosphorous tetriodide is brought into contact with glycerin, an energetic reaction ensues, allylic iodide being formed:—

$$\underset{\text{Diphosphorus tetriodide.}}{{}'\mathbf{P}''_2\mathrm{I}_4} + 2\underset{\text{Glycerin.}}{\left\{\begin{array}{l}\mathbf{CH}_2\mathrm{Ho}\\ \mathbf{CH}\mathrm{Ho}\\ \mathbf{CH}_2\mathrm{Ho}\end{array}\right.} = 2\underset{\text{Allylic iodide.}}{{}''\left\{\begin{array}{l}\mathbf{CH}_2\\ \mathbf{CH}\\ \mathbf{CH}_2\mathrm{I}\end{array}\right.} + \underset{\text{Phosphorus acid.}}{2\mathbf{P}\mathrm{OHHo}_2} + \mathrm{I}_2.$$

Relations of Glycerin to Propylic Glycol.

The several semimolecules of hydroxyl in glycerin are capable of being replaced by chlorine, bromine, &c.; thus, by the action of hydrochloric acid on glycerin, one semimolecule of hydroxyl is displaced by chlorine, monochlorhydrin being formed:—

$$\underset{\text{Glycerin.}}{\left\{\begin{array}{l}\mathbf{CH}_2\mathrm{Ho}\\ \mathbf{CH}\mathrm{Ho}\\ \mathbf{CH}_2\mathrm{Ho}\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}} = \underset{\text{Monochlorhydrin.}}{\left\{\begin{array}{l}\mathbf{CH}_2\mathrm{Cl}\\ \mathbf{CH}\mathrm{Ho}\\ \mathbf{CH}_2\mathrm{Ho}\end{array}\right.} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2}.$$

Monochlorhydrin is identical with monochlorinated propylic glycol:—

$$\underset{\text{Monochlorhydrin.}}{\left\{\begin{array}{l} CH_2Cl \\ CHHo \\ CH_2Ho \end{array}\right.} = \underset{\substack{\text{Monochlorinated} \\ \text{propylic glycol.}}}{\left\{\begin{array}{l} C(CH_2Cl)HHo \\ CH_2Ho \end{array}\right.} .$$

By the action of sodium amalgam and water, monochlorinated propylic glycol is readily converted into propylic glycol:—

$$\underset{\substack{\text{Monochlorinated} \\ \text{propylic glycol.}}}{\left\{\begin{array}{l} C(CH_2Cl)HHo \\ CH_2Ho \end{array}\right.} + H_2 = \underset{\substack{\text{Propylic} \\ \text{glycol.}}}{\left\{\begin{array}{l} C(CH_3)HHo \\ CH_2Ho \end{array}\right.} + \underset{\substack{\text{Hydrochloric} \\ \text{acid.}}}{HCl.}$$

Relations of Glycerin to the Trihydric Acids—Glyceric Acid and Tartronic Acid.

By the slow action of nitric acid, glycerin is converted into glyceric acid:—

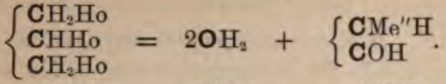
$$\underset{\text{Glycerin.}}{\left\{\begin{array}{l} CH_2Ho \\ CHHo \\ CH_2Ho \end{array}\right.} + O_2 = \underset{\substack{\text{Glyceric} \\ \text{acid.}}}{\left\{\begin{array}{l} CH_2Ho \\ CHHo \\ COHo \end{array}\right.} + \underset{\text{Water.}}{OH_2.}$$

A second semimolecule of oxatyl has not been produced in glycerin, so as to convert the latter into a dibasic acid; but there can be little doubt that tartronic acid, which is formed by the spontaneous decomposition of nitrotartaric acid, is the acid in question, and that it has the following constitution:—

$$\underset{\text{Tartronic acid.}}{\left\{\begin{array}{l} COHo \\ CHHo. \\ COHo \end{array}\right.}$$

Relations of Glycerin to Acrylic Acid.

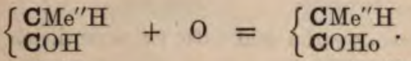
By the action of substances having an affinity for water, such as phosphoric anhydride or sulphuric acid, glycerin is converted into acrolein:—



$$\left\{\begin{matrix}CH_2Ho\\ CHHo\\ CH_2Ho\end{matrix}\right. = 2OH_2 + \left\{\begin{matrix}CMe''H\\ COH\end{matrix}\right. .$$

Glycerin. Water. Acrolein.

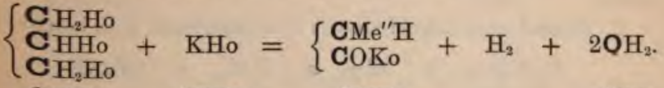
By the absorption of oxygen, acrolein is transformed into acrylic acid:—



$$\left\{\begin{matrix}CMe''H\\ COH\end{matrix}\right. + O = \left\{\begin{matrix}CMe''H\\ COHo\end{matrix}\right. .$$

Acrolein. Acrylic acid.

Both these reactions are accomplished simultaneously when glycerin is added to fused potassic hydrate:—



$$\left\{\begin{matrix}CH_2Ho\\ CHHo\\ CH_2Ho\end{matrix}\right. + KHo = \left\{\begin{matrix}CMe''H\\ COKo\end{matrix}\right. + H_2 + 2OH_2.$$

Glycerin. Potassic hydrate. Potassic acrylate. Water.

CHAPTER XII.

TRIHYDRIC ALCOHOLS.

Pyrogallic or $C_nH_{2n-9}Ho_3$ series.

Like the phenyl and orcin series, these alcohols are the direct derivatives of benzene. The three hydroxyl groups replace hydrogen atoms of the nucleus.

The following bodies are believed to belong to this series, whilst several other compounds not yet sufficiently known will probably soon be added to it:—

		Melting-point.
Pyrogallin.	$C_6H_3Ho_3$	115°.
Phloroglucin.		220
Phenomalic acid ?		—

PYROGALLIN, *Pyrogallic Acid.*

$C_6H_3Ho_3$.

Melts at 115°. *Sublimes with partial decomposition at* 210°.

Preparation.—1. By heating gallic acid to 210°—220° in a stream of carbonic anhydride:—

$$\underset{\text{Gallic acid.}}{\left\{\begin{matrix}C_6H_2Ho_3\\COHo\end{matrix}\right.} = \underset{\text{Pyrogallin.}}{C_6H_3Ho_3} + CO_2.$$

2. By heating gallic acid with twice or thrice its weight of water to 200°—210° for half an hour in a Papin's digester. The reaction is the same as in No. 1.

Reactions.—1. Does not neutralize alkalies or form true salts.

2. Passed over heated zinc, it is transformed into benzol:—

$$\underset{\text{Pyrogallin.}}{C_6H_3Ho_3} + 3Zn = \underset{\text{Benzol.}}{C_6H_6} + 3ZnO.$$

3. Bromine converts pyrogallin into tribromopyrogallin:—

$$\underset{\text{Pyrogallin.}}{C_6H_3Ho_3} + 3Br_2 = \underset{\text{Tribromopyrogallin.}}{C_6Br_3Ho_3} + 3HBr.$$

4. Heated to 250°, it yields water and metagallic acid:—

$$\underset{\text{Pyrogallin.}}{C_6H_3Ho_3} = \underset{\text{Metagallic acid.}}{C_6H_3OHo} + OH_2.$$

5. Ammonia in the presence of air forms with it pyrogallein, to which the formula $C_{18}H_{20}N_6O_{10}$ has been assigned.

6. Concentrated boiling solution of caustic potash decomposes it into acetic, oxalic, and carbonic acids.

7. An alkaline solution of pyrogallin rapidly absorbs free oxygen, forming a dark-coloured body, together with acetic and carbonic acids and a small quantity of carbonic oxide.

OTHER POLYHYDRIC ALCOHOLS.

Erythrite (Erythroglucin, Erythromannite, Phycite, Pseudorcin) is a tetrahydic alcohol; and the acid corresponding to it is tartaric acid. Citric acid may also be considered as derived from an unknown alcohol of this series. A glance at the formulæ of these alcohols and acids will show their relations:—

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{H_2Ho}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right. . \quad \left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right. . \quad \Bigg| \quad \left\{\begin{array}{l}\mathbf{C}\mathrm{H_2(}\mathbf{C}\mathrm{H_2Ho)}\\ \mathbf{C}\mathrm{Ho(}\mathbf{C}\mathrm{H_2Ho)}\\ \mathbf{C}\mathrm{H_2(}\mathbf{C}\mathrm{H_2Ho)}\end{array}\right. . \quad \left\{\begin{array}{l}\mathbf{C}\mathrm{H_2(}\mathbf{C}\mathrm{OHo)}\\ \mathbf{C}\mathrm{Ho(}\mathbf{C}\mathrm{OHo)}\\ \mathbf{C}\mathrm{H_2(}\mathbf{C}\mathrm{OHo)}\end{array}\right. .$$

Erythrite. Tartaric acid. Tetrahydric alcohol (unknown). Citric acid.

When reduced by hydriodic acid, erythrite yields secondary butylic iodide:—

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{H_2Ho}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right. + \quad 7\mathrm{HI} \quad = \quad 4\mathbf{O}\mathrm{H_2} \quad + \quad \left\{\begin{array}{l}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{H_2}\\ \mathbf{C}\mathrm{HI}\\ \mathbf{C}\mathrm{H_3}\end{array}\right. + \ 3\mathrm{I_2}.$$

Erythrite. Hydriodic acid. Water. Secondary butylic iodide.

Aposorbic acid may be regarded as derived by oxidation from an unknown pentahydric alcohol:—

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{H_2Ho}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}.\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right. \qquad \left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}.\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$$

Unknown pentahydric alcohol. Aposorbic acid.

Mannite is a hexahydric alcohol. There are three acids corresponding to this alcohol: these are saccharic and mucic acids, which are isomeric, and mannitic acid:—

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{H_2Ho}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\cdot\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right. \qquad \left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\cdot\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right. \qquad \left\{\begin{array}{l}\mathbf{C}\mathrm{H_2Ho}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\cdot\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$$

Mannite. Saccharic or mucic acid. Mannitic acid.

Mannite is closely related to *glucose*, the latter containing two atoms of hydrogen less than the former. Glucose can, in fact, be converted into mannite by the action of nascent hydrogen:—

$$\underset{\text{Glucose.}}{\left\{\begin{array}{l}CH_2Ho\\ CHHo\\ CHHo\\ CHHo\\ CHHo\\ COH\end{array}\right.} + H_2 = \underset{\text{Mannite.}}{\left\{\begin{array}{l}CH_2Ho\\ CHHo\\ CHHo\\ CHHo\\ CHHo\\ CH_2Ho\end{array}\right.}$$

Alcohols of high hydricity possess a sweet taste, in fact with increase of hydricity the alcohols gradually pass into saccharine substances or sugars.

CHAPTER XIII.

THE ETHERS.

These compounds are the oxides of the positive radicals.

Each series of alcohols produces a series of ethers; we have thus ethers of the monohydric, dihydric, and trihydric alcohols, of which the following are the general formulæ:—

	Methyl series.	Vinyl or Allyl series.	Phenyl series.
Ethers of the monohydric alcohols	$\left\{\begin{array}{l}C_nH_{2n+1}\\ O\\ C_nH_{2n+1}\end{array}\right.$	$\left\{\begin{array}{l}C_nH_{2n-1}\\ O\\ C_nH_{2n-1}\end{array}\right.$	$\left\{\begin{array}{l}C_nH_{2n-7}\\ O\\ C_nH_{2n-7}\end{array}\right.$

Ethers of the dihydric alcohols $C_nH_{2n}O$.

Ethers of the trihydric alcohols $\left\{\begin{array}{l}C_nH_{2n}\ \text{-}O\text{-}H_{2n}\ \ C_n\\ C_nH_{2n-1}\text{-}O\text{-}H_{2n-1}C_n\\ C_nH_{2n}\ \text{-}O\text{-}H_{2n}\ \ C_n\end{array}\right\}$.

ETHERS OF THE MONOHYDRIC ALCOHOLS.

These bodies are derived from the alcohols by the substitution of the hydroxylic hydrogen contained in the latter by *a positive* monad radical.

METHYL SERIES.

The following list contains some of the ethers of this series:—

						Boiling-points.
Methylic ether ……………			$\left\{\begin{matrix}CH_3\\O\\CH_3\end{matrix}\right.$	or	OMe_2	$-21°$
Methylicethylic ether	$\left\{\begin{matrix}CH_3\\O\\C_2H_5\end{matrix}\right.$	or	$\left\{\begin{matrix}CH_3\\O\\CMeH_2\end{matrix}\right.$	or	$OMeEt$	$+11$
Ethylic ether…….	$\left\{\begin{matrix}C_2H_5\\O\\C_2H_5\end{matrix}\right.$	or	$\left\{\begin{matrix}CMeH_2\\O\\CMeH_2\end{matrix}\right.$	or	OEt_2	35·6
Methylicamylic ether	$\left\{\begin{matrix}CH_3\\O\\C_5H_{11}\end{matrix}\right.$	or	$\left\{\begin{matrix}CH_3\\O\\CBuH_2\end{matrix}\right.$	or	$OMeAy$	92
Ethylic butylic ether	$\left\{\begin{matrix}C_2H_5\\O\\C_4H_9\end{matrix}\right.$	or	$\left\{\begin{matrix}CMeH_2\\O\\CPrH_2\end{matrix}\right.$	or	$OEtBu$	80?
Ethylic amylic ether	$\left\{\begin{matrix}C_2H_5\\O\\C_5H_{11}\end{matrix}\right.$	or	$\left\{\begin{matrix}CMeH_2\\O\\CBuH_2\end{matrix}\right.$	or	$OEtAy$	112
Butylic ether…….	$\left\{\begin{matrix}C_4H_9\\O\\C_4H_9\end{matrix}\right.$	or	$\left\{\begin{matrix}CPrH_2\\O\\CPrH_2\end{matrix}\right.$	or	OBu_2	104
Amylic ether…….	$\left\{\begin{matrix}C_5H_{11}\\O\\C_5H_{11}\end{matrix}\right.$	or	$\left\{\begin{matrix}CBuH_2\\O\\CBuH_2\end{matrix}\right.$	or	OAy_2	176

Formation.—1. By the action of sulphuric acid upon the $C_nH_{2n+1}Ho$ alcohols. The process may be divided into the two following stages:—

$$\underset{\text{Alcohol.}}{C_nH_{2n+1}Ho} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Sulpho-acid.}}{SO_2Ho(C_nH_{2n+1}O)} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\text{Sulpho-acid.}}{SO_2Ho(C_nH_{2n+1}O)} + \underset{\text{Alcohol.}}{C_nH_{2n+1}Ho} = \underset{\text{Ether.}}{\left\{\begin{matrix}C_nH_{2n+1}\\O\\C_nH_{2n+1}\end{matrix}\right.} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2}.$$

2. By converting the $C_nH_{2n+1}Ho$ alcohols into sodium or potassium compounds, and then acting upon the latter with the iodides of the monad positive radicals:—

$$\underset{\text{Alcohol.}}{2C_nH_{2n+1}Ho} + Na_2 = \underset{\text{Sodic ethylate.}}{2C_nH_{2n+1}Nao} + H_2.$$

$$\underset{\text{Sodic ethylate.}}{C_nH_{2n+1}Nao} + \underset{\text{Iodide.}}{C_nH_{2n+1}I} = \underset{\text{Ether.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ O\\ C_nH_{2n+1}\end{matrix}\right.} + \underset{\text{Sodic iodide.}}{NaI.}$$

Reaction.—The ethers can be reconverted into the corresponding alcohols by treating them with sulphuric acid, and then distilling with water the sulpho-acid so produced :—

$$\underset{\text{Ether.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ O\\ C_nH_{2n+1}\end{matrix}\right.} + \underset{\text{Sulphuric acid.}}{2\mathbf{S}O_2Ho} = \underset{\text{Sulpho-acid.}}{2\mathbf{S}O_2Ho(C_nH_{2n+1}O)} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

$$\underset{\text{Sulpho-acid.}}{\mathbf{S}O_2Ho(C_nH_{2n+1}O)} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} + \underset{\text{Alcohol.}}{C_nH_{2n+1}Ho.}$$

METHYLIC ETHER, *Methylic Oxide.*

$$\left\{\begin{matrix}\mathbf{C}H_3\\ O\\ \mathbf{C}H_3\end{matrix}\right. \text{ or } \mathbf{O}Me_2.$$

Molecular weight $=46$. *Molecular volume* $\square\!\square$. 1 *litre of methylic ether vapour weighs* 23 *criths. Boils at* $-21°$.

Preparation.—By heating methylic alcohol with sulphuric acid or boric anhydride :—

$$\underset{\text{Methylic alcohol.}}{\mathbf{C}H_3Ho} + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} = \underset{\text{Sulphomethylic acid.}}{\mathbf{S}O_2Ho(CH_3O)} + \underset{\text{Water.}}{\mathbf{O}H_2;}$$

$$\underset{\text{Sulphomethylic acid.}}{\mathbf{S}O_2Ho(CH_3O)} + \underset{\text{Methylic alcohol.}}{\mathbf{C}H_3Ho} = \underset{\text{Methylic ether.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ O\\ \mathbf{C}H_3\end{matrix}\right.} + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2.}$$

Reaction.—Methylic ether is acted upon by chlorine under the influence of light, the hydrogen being displaced atom for atom by chlorine. The following compounds are formed :—

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{H_2Cl}\\ \mathrm{O}\\ \mathbf{C}\mathrm{H_2Cl}\end{array}\right. ;\qquad \left\{\begin{array}{l}\mathbf{C}\mathrm{HCl_2}\\ \mathrm{O}\\ \mathbf{C}\mathrm{HCl_2}\end{array}\right. ;\qquad \left\{\begin{array}{l}\mathbf{C}\mathrm{Cl_3}\\ \mathrm{O}\\ \mathbf{C}\mathrm{Cl_3}\end{array}\right. .$$

Dichlorinated methylic ether.	Tetrachlorinated methylic ether.	Perchlorinated methylic ether.

ETHYLIC ETHER, *Ethylic Oxide, Ether, Sulphuric Ether.*

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{MeH_2}\\ \mathrm{O}\\ \mathbf{C}\mathrm{MeH_2}\end{array}\right. \text{ or } \mathbf{O}\mathrm{Et_2}.$$

Molecular weight = 74. *Molecular volume* $\square\square$. 1 *litre of ether vapour weighs* 37 *criths. Sp. gr.* = 0·723. *Boils at* 35°·6.

Preparation.—A mixture of equal volumes of sulphuric acid and alcohol is heated to a temperature of from 140—145°, and a constant stream of alcohol is allowed to flow into the mixture. Ether and water distil over together. Two reactions take place successively: in the first, the alcohol is converted into sulphovinic acid; and in the second, the sulphovinic acid is converted by a further quantity of alcohol into sulphuric acid and ether:—

$$\underset{\text{Alcohol.}}{\mathrm{EtHo}} + \underset{\text{Sulphuric acid.}}{\mathbf{S}\mathrm{O_2Ho_2}} = \underset{\text{Sulphovinic acid.}}{\mathbf{S}\mathrm{O_2EtoHo}} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H_2}}.$$

$$\underset{\text{Sulphovinic acid.}}{\mathbf{S}\mathrm{O_2EtoHo}} + \underset{\text{Alcohol.}}{\mathrm{EtHo}} = \underset{\text{Ether.}}{\mathbf{O}\mathrm{Et_2}} + \underset{\text{Sulphuric acid.}}{\mathbf{S}\mathrm{O_2Ho_2}}.$$

In this manner the same quantity of sulphuric acid can convert an unlimited quantity of alcohol into ether.

The formation of ether is not due to the simple removal of water from two molecules of alcohol by sulphuric acid. This is proved, first, by the sulphuric acid not becoming more dilute, and, secondly, by the fact that, if sulphamylic acid be acted upon by ethylic alcohol, the mixed ethylic amylic ether is formed:—

$$\underset{\text{Sulphamylic acid.}}{\mathbf{S}\mathrm{O_2AyoHo}} + \underset{\text{Ethylic alcohol.}}{\mathrm{EtHo}} = \underset{\text{Sulphuric acid.}}{\mathbf{S}\mathrm{O_2Ho_2}} + \underset{\text{Ethylic amylic ether.}}{\mathbf{O}\mathrm{AyEt}}.$$

Reactions.—1. Ethylic ether, when mixed with an equ volume of sulphuric acid, produces sulphovinic acid:—

$$\underset{\text{Ethylic ether.}}{\mathbf{O}Et_2} + \underset{\text{Sulphuric acid.}}{2\mathbf{S}O_2Ho_2} = \underset{\text{Sulphovinic acid.}}{2\mathbf{S}O_2EtoHo} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

2. Hot nitric acid converts ethylic ether into carbon acetic, and oxalic acids.

3. Exposed to the air it gradually absorbs oxygen, and transformed into acetic acid:—

$$\underset{\text{Ethylic ether.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2\\ O\\ \mathbf{C}H_2\\ \mathbf{C}H_3\end{matrix}\right.} + 2O_2 = \underset{\text{Acetic acid.}}{2\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

ETHYLIC SULPHIDE, *Sulphur Ether.*

$$\left\{\begin{matrix}\mathbf{C}MeH_2\\ S\\ \mathbf{C}MeH_2\end{matrix}\right. \text{ or } \mathbf{S}Et_2.$$

Molecular weight = 90. *Molecular volume* $\square\!\square$. 1 *litre of ethylic sulphide vapour weighs* 45 *criths. Boils at* 91°.

Preparation.—By adding ethylic chloride to potassic sulphide, and distilling:—

$$\underset{\text{Ethylic chloride.}}{2\mathbf{C}MeH_2Cl} + \underset{\text{Potassic sulphide.}}{\mathbf{S}K_2} = \underset{\text{Ethylic sulphide.}}{\left\{\begin{matrix}\mathbf{C}MeH_2\\ S\\ \mathbf{C}MeH_2\end{matrix}\right.} + \underset{\text{Potassic chloride.}}{2KCl.}$$

Reactions.—1. Ethylic sulphide combines directly with ethylic iodide, forming

Sulphurous triethylo-iodide …… $\mathbf{S}Et_3I$.

By the action of argentic oxide on this iodide, the corresponding hydrate may be formed:—

$$\underset{\text{Sulphurous triethylo-iodide.}}{\mathbf{S}Et_3I} + \underset{\text{Argentic hydrate.}}{AgHo} = \underset{\text{Sulphurous triethylo-hydrate.}}{\mathbf{S}Et_3Ho} + \underset{\text{Argentic iodide.}}{AgI.}$$

2. By cold nitric acid it is converted into sulphurous diethoxide ($SOEt_2$), which by more powerful oxidizing agents is transformed into diethylsulphone (sulphuric diethoxide), SO_2Et_2, which melts at 70°, and boils at 248°.

ETHERS OF THE VINYL AND PHENYL SERIES.

Of the ethers of the vinyl series, allylic ether $\left\{\begin{matrix} C_3H_5 \\ O \\ C_3H_5 \end{matrix}\right.$, alone is known. It boils at 82°. Two mixed ethers, vinyl-ethyl ether, $\left\{\begin{matrix} C_2H_3 \\ O \\ C_2H_5 \end{matrix}\right.$, and allyl-ethyl ether, $\left\{\begin{matrix} C_3H_5 \\ O \\ C_2H_5 \end{matrix}\right.$, have been prepared.

In the phenyl series, phenylic ether, $\left\{\begin{matrix} C_6H_5 \\ O \\ C_6H_5 \end{matrix}\right.$, and benzylic ether, $\left\{\begin{matrix} C_7H_7 \\ O \\ C_7H_7 \end{matrix}\right.$, have been obtained.

By digesting benzylic chloride with potassic phenylate, a mixed ether, phenyl-benzyl ether, is formed :—

$$\underset{\text{Benzylic chloride.}}{\left\{\begin{matrix} C_6H_5 \\ CH_2Cl \end{matrix}\right.} \quad + \quad \underset{\text{Potassic phenylate.}}{C_6H_5Ko} \quad = \quad \underset{\text{Potassic chloride.}}{KCl} \quad + \quad \underset{\text{Phenyl-benzyl ether.}}{\left\{\begin{matrix} C_6H_5 \\ CH_2 \\ O \\ C_6H_5 \end{matrix}\right.}\ .$$

ETHERS OF THE DIHYDRIC ALCOHOLS.

Of these the four following are known, but the first only has been carefully studied :—

	Boiling-points.
Ethylenic oxide, C_2H_4O	13·5°
Propylenic oxide, C_3H_6O	35·0
Amylenic oxide, $C_5H_{10}O$	95·0
Phenylenic oxide $\left\{\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\right. O$ (fuses at 80°·5)	287·5

ETHYLENIC OXIDE, *Ethylenic Ether.*

$$C_2H_4O = \left\{\begin{array}{l}CH_2\\CH_2\end{array}\right.O.$$

Molecular weight = 44. *Molecular volume* $\square\square$. 1 *litre of ethylenic oxide vapour weighs* 22 *criths. Boils at* 13°·5.

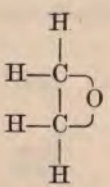
Preparation.—Ethylenic oxide is obtained from glycol by converting the latter, first into ethylenic chlorhydrate, or chlorhydric glycol, by the action of hydrochloric acid, and subsequently treating the compound thus formed with potassic hydrate:—

$$\underset{\text{Glycol.}}{\left\{\begin{array}{l}CH_2Ho\\CH_2Ho\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ethylenic chlorhydrate.}}{\left\{\begin{array}{l}CH_2Ho\\CH_2Cl\end{array}\right.} + \underset{\text{Water.}}{OH_2}:$$

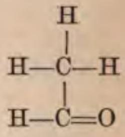
$$\underset{\text{Ethylenic chlorhydrate.}}{\left\{\begin{array}{l}CH_2Ho\\CH_2Cl\end{array}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Ethylenic oxide.}}{\left\{\begin{array}{l}CH_2\\CH_2\end{array}\right.O} + \underset{\text{Water.}}{OH_2} + \underset{\text{Potassic chloride.}}{KCl.}$$

Isomers.—Ethylenic oxide is isomeric with acetic aldehyde. The nature of this isomerism is seen in the following formulæ:—

$$\underset{\text{Ethylenic oxide.}}{\left\{\begin{array}{l}CH_2\\CH_2\end{array}\right.O.}$$



$$\underset{\text{Acetic aldehyde.}}{\left\{\begin{array}{l}CH_3\\COH\end{array}\right.}\cdot$$



Reactions.—1. Ethylenic oxide unites with nascent hydrogen, forming alcohol:—

$$\underset{\text{Ethylenic oxide.}}{\left\{\begin{array}{l}CH_2\\CH_2\end{array}\right.O} + H_2 = \underset{\text{Alcohol.}}{\left\{\begin{array}{l}CH_3\\CH_2Ho\end{array}\right.}\cdot$$

2. It also unites with oxygen, forming glycollic acid:—

$$\underset{\text{Ethylenic oxide.}}{\left\{\begin{array}{l}CH_2\\CH_2\end{array}\right.O} + O_2 = \underset{\text{Glycollic acid.}}{\left\{\begin{array}{l}CH_2Ho\\COHo\end{array}\right.}\cdot$$

3. It is a basic substance, and unites directly with acids:—

$$\underset{\substack{\text{Ethylenic}\\\text{oxide.}}}{\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.O} + \underset{\substack{\text{Hydro-}\\\text{chloric}\\\text{acid.}}}{HCl} = \underset{\substack{\text{Ethylenic}\\\text{chlorhydrate}\\\text{or chlorhydric}\\\text{glycol.}}}{\left\{\begin{matrix}CH_2Cl\\CH_2Ho\end{matrix}\right.}$$

4. Ethylenic oxide precipitates as hydrates many metals from solutions of their salts, such as the ferric, aluminic, cupric, and magnesic hydrates:—

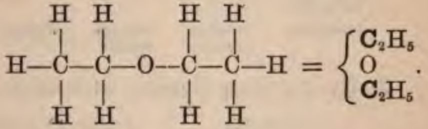
$$2\underset{\substack{\text{Ethylenic}\\\text{oxide.}}}{\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.O} + \underset{\substack{\text{Magnesic}\\\text{chloride.}}}{MgCl_2} + \underset{\text{Water.}}{2OH_2} = 2\underset{\substack{\text{Ethylenic}\\\text{chlorhydrate.}}}{\left\{\begin{matrix}CH_2Cl\\CH_2Ho\end{matrix}\right.} + \underset{\substack{\text{Magnesic}\\\text{hydrate.}}}{MgHo_2}.$$

5. It also combines directly with water, reproducing glycol:—

$$\underset{\substack{\text{Ethylenic}\\\text{oxide.}}}{\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.O} + \underset{\text{Water.}}{OH_2} = \underset{\text{Glycol.}}{\left\{\begin{matrix}CH_2Ho\\CH_2Ho\end{matrix}\right.}$$

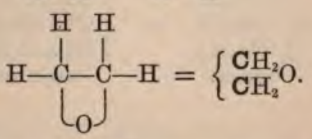
These reactions exhibit a wide difference between the behaviour of ethylenic ether and that of ethylic ether. This difference arises from the fact, that in ethylic ether the ethyl semimolecules are held together by the oxygen only, whereas in ethylenic ether the linking of the two groups of CH_2 does not depend on the oxygen atom alone, as will be seen from the following formulæ:—

Ethylic ether ......



$$\begin{matrix} & H & & H & & & & H & & H & \\ & | & & | & & & & | & & | & \\ H- & C & - & C & -O- & & & C & - & C & -H \\ & | & & | & & & & | & & | & \\ & H & & H & & & & H & & H & \end{matrix} = \left\{\begin{matrix}C_2H_5\\O\\C_2H_5\end{matrix}\right..$$

Ethylenic ether ....



$$\begin{matrix} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & \llcorner & O & \lrcorner & \end{matrix} = \left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.O.$$

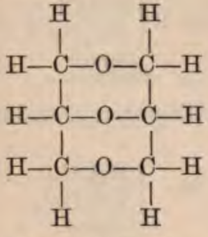
On account of this peculiarity of constitution, ethylenic oxide can combine directly with many substances without the disruption of its molecule,—a property which obviously cannot be possessed by ethylic ether.

ETHERS OF THE TRIHYDRIC ALCOHOLS.

Of these only one is known, viz.:—

GLYCYLIC ETHER, *Glycylic Oxide.*

Boils at 172°.



$$= \left\{\begin{array}{l} \mathbf{CH_2\text{-}O\text{-}H_2C} \\ \mathbf{CH\ \text{-}O\text{-}H\ C} \\ \mathbf{CH\ \text{-}O\text{-}H_2C} \end{array}\right\}.$$

Preparation.—1. By the action of potassic hydrate on so-called iodhydrin:—

$$\left\{\begin{array}{l} \left.\begin{array}{l}\mathbf{CH_2}\\ \mathbf{CH_2}\end{array}\right. O \\ \mathbf{CH_2} \\ O \\ \mathbf{CH_2} \\ \mathbf{CHI} \\ \mathbf{CH_2}Ho \end{array}\right. + KHo = KI + \mathbf{OH_2} + \left\{\begin{array}{l} \mathbf{CH_2\text{-}O\text{-}H_2C} \\ \mathbf{CH\ \text{-}O\text{-}H\ C} \\ \mathbf{CH_2\text{-}O\text{-}H_2C} \end{array}\right\}.$$

Iodhydrin. Potassic hydrate. Potassic iodide. Water. Glycylic ether.

2. By distilling glycerin with calcic chloride:—

$$2\left\{\begin{array}{l} \mathbf{CH_2}Ho \\ \mathbf{CH}Ho \\ \mathbf{CH_2}Ho \end{array}\right. = \left\{\begin{array}{l} \mathbf{CH_2\text{-}O\text{-}H_2C} \\ \mathbf{CH\ \text{-}O\text{-}H\ C} \\ \mathbf{CH_2\text{-}O\text{-}H_2C} \end{array}\right\} + 3\mathbf{O}H_2.$$

Glycerin. Glycylic ether. Water.

CHAPTER XIV.

THE HALOID ETHERS.

Each series of positive radicals forms its own series of haloid ethers.

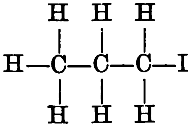
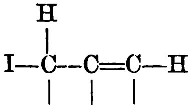
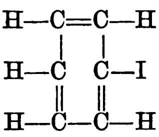
These ethers are produced by the substitution of hydroxyl in the alcohols by chlorine, bromine, iodine, fluorine, or cyanogen.

Haloid Ethers of the Monad Positive Radicals.

As these radicals can unite with only one semimolecule of hydroxyl, they can form only one haloid ether. Each series of radicals therefore forms one series of haloid ethers:—

I. Haloid ethers of the form $C_nH_{2n+1}Cl$.
II. „ „ „ „ $C_nH_{2n-1}Cl$.
III. „ „ „ „ $C_nH_{2n-7}Cl$.

The following will serve as examples of the three series:—

Propylic iodide..	C_3H_7I or $C(C_2H_5)H_2I$.	 $\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & \vert & & \vert & & \vert & & \\ H & — & C & — & C & — & C & — & I \\ & & \vert & & \vert & & \vert & & \\ & & H & & H & & H & & \end{array}$
Allylic iodide ..	C_3H_5I or $C(C_2H_3)H_2I$.	 $\begin{array}{ccccccccc} & & H & & & & & & \\ & & \vert & & & & & & \\ I & — & C & — & C & = & C & — & H \\ & & \vert & & \vert & & \vert & & \\ & & H & & H & & H & & \end{array}$
Phenylic iodide..	C_6H_5I	

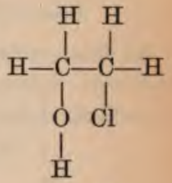
Haloid Ethers of the Dyad Positive Radicals.

As the dihydric alcohols contain two semimolecules of hydroxyl, it follows that there are two classes of haloid ethers derivable from them. The first is formed by the substitution of one of the semimolecules of hydroxyl by chlorine, bromine, &c., and the second by the like displacement of both semimolecules of hydroxyl:—

I. Haloid ethers of the form $\mathbf{C}_nH_{2n}HoCl$.
II. ,, ,, ,, ,, $\mathbf{C}_nH_{2n}Cl_2$.

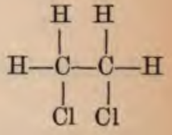
The following examples will suffice to illustrate the constitution of both these classes of haloid ethers:—

Chlorhydric glycol or ethylenic chlorhydrate...... $\mathbf{C}_2H_4HoCl$ or $\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Cl\end{array}\right.$.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & O & & Cl & & \\ & & | & & & & \\ & & H & & & & \end{array}$$

Ethylenic dichloride...... $\mathbf{C}_2H_4Cl_2$ or $\left\{\begin{array}{l}\mathbf{C}H_2Cl\\ \mathbf{C}H_2Cl\end{array}\right.$.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & Cl & & Cl & & \end{array}$$

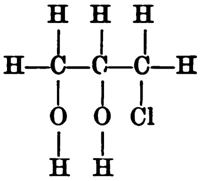
Haloid Ethers of the Triad Positive Radicals.

Three classes of haloid ethers are derived from the trihydric alcohols by the successive substitution of the three semimolecules of hydroxyl contained in these alcohols by chlorine, bromine, &c. A fourth class also exists, which stands intermediate between the ethers and the haloid ethers, and which is formed by the substitution of one of the semimolecules of hydroxyl in the alcohol by a monad negative radical, such as chlorine, bromine, or cyanogen, and the remaining two semimolecules of hydroxyl by a dyad oxygen:—

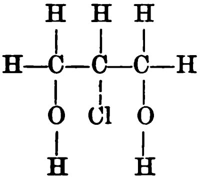
I. Haloid ethers of the form $C_nH_{2n-1}Ho_2Cl$.
II. ,, ,, ,, $C_nH_{2n-1}HoCl_2$.
III. ,, ,, ,, $C_nH_{2n-1}Cl_3$.
IV. ,, ,, ,, $C_nH_{2n-1}OCl$.

The following are examples of each of these classes :—

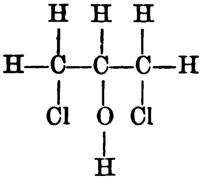
α-Chlorhydrin $\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CHHo}\\ \mathrm{CH_2Cl}\end{array}\right.$



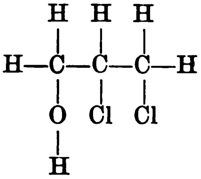
β-Chlorhydrin $\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CHCl}\\ \mathrm{CH_2Ho}\end{array}\right.$



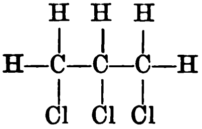
α-Dichlorhydrin $\left\{\begin{array}{l}\mathrm{CH_2Cl}\\ \mathrm{CHHo.}\\ \mathrm{CH_2Cl}\end{array}\right.$



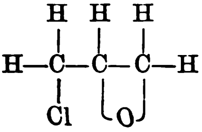
β-Dichlorhydrin $\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CHCl}\\ \mathrm{CH_2Cl}\end{array}\right.$



Trichlorhydrin $\left\{\begin{array}{l}\mathrm{CH_2Cl}\\ \mathrm{CHCl\ .}\\ \mathrm{CH_2Cl}\end{array}\right.$



Hydrochloric glycide or epichlorhydrin . . $\left\{\begin{array}{l}\mathrm{CH_2Cl}\\ \begin{array}{l}\mathrm{CH}\\ \mathrm{CH_2}\end{array}\mathrm{O.}\end{array}\right.$



HALOID ETHERS OF THE MONAD POSITIVE RADICALS.

Preparation.—These ethers are produced by the following general reactions:—

1. By the action of the hydracids upon the alcohols:—

$$\underset{\text{Alcohol.}}{C_nH_{2n+1}Ho} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Haloid ether.}}{C_nH_{2n+1}Cl} + \underset{\text{Water.}}{OH_2}.$$

This reaction does not apply to the phenols.

2. By the action of phosphorous chloride on the alcohols:—

$$\underset{\text{Alcohol.}}{3C_nH_{2n+1}Ho} + \underset{\text{Phosphorous chloride.}}{PCl_3} = \underset{\text{Haloid ether.}}{3C_nH_{2n+1}Cl} + \underset{\text{Phosphorous acid.}}{POHHo_2}.$$

3. By the action of chlorine on the hydrides of the radicals:—

$$\underset{\text{Hydride.}}{C_nH_{2n+1}H} + Cl_2 = \underset{\text{Haloid ether.}}{C_nH_{2n+1}Cl} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

It is obvious that in these reactions bromine and iodine may be used instead of chlorine.

These reactions, except No. 1, apply equally to the C_nH_{2n-1} and C_nH_{2n-7} series.

For the preparation of the nitriles, which are isomeric with the cyanides of the radicals, two special reactions (Nos. 1 and 2) are employed.

1. The distillation in the dry state of a mixture of the potassic sulphate of the radical with potassic cyanide:—

$$\underset{\text{Potassic sulphate of the radical.}}{SO_2Ko(C_nH_{2n+1}O)} + \underset{\text{Potassic cyanide.}}{KCy} = \underset{\text{Potassic sulphate.}}{SO_2Ko_2} + \underset{\text{Abnormal cyanide or nitrile.}}{C_nH_{2n+1}Cy}.$$

2. The fatty acids are converted into ammonium salts and distilled with phosphoric anhydride, when the abnormal cyanides, or nitriles, of the positive radicals which they contain, are produced:—

$$\underset{\text{Ammonium salt.}}{\left\{\begin{matrix} C_nH_{2n+1} \\ \mathbf{C}O(N^{v}H_4O)\end{matrix}\right.} + \underset{\text{Phosphoric anhydride.}}{2\mathbf{P}_2O_5} = \underset{\text{Abnormal cyanide or nitrile.}}{\left\{\begin{matrix} C_nH_{2n+1} \\ \mathbf{C}N'''\end{matrix}\right.} + \underset{\text{Metaphosphoric acid.}}{4\mathbf{P}O_2Ho.}$$

3. By the action of chloroform on an amine in the presence of an alcoholic solution of potassic hydrate, a normal cyanide is produced. These cyanides are isomeric with those obtained by the two previous processes, and appear to contain nitrogen in the pentad condition:—

$$\underset{\text{Amine.}}{\left\{\begin{matrix} C_nH_{2n+1} \\ \mathbf{N}H_2\end{matrix}\right.} + \underset{\text{Chloroform.}}{\mathbf{C}HCl_3} = \underset{\text{Hydrochloric acid.}}{3HCl} + \underset{\text{Cyanide.}}{\left\{\begin{matrix} \mathbf{C}_nH_{2n+1} \\ \mathbf{N}C\end{matrix}\right.}.$$

Reactions.—1. Treated with alcoholic solution of potash, most of the haloid ethers of the C_nH_{2n+1} series, except the cyanides, are reconverted into alcohols:—

$$\underset{\text{Haloid ether.}}{C_nH_{2n+1}Cl} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Alcohol.}}{C_nH_{2n+1}Ho} + \underset{\text{Potassic chloride.}}{KCl.}$$

2. The nitriles, or abnormal cyanides, under similar circumstances are converted into potassic salts of the acids which contain the positive radical of the cyanide:—

$$\underset{\text{Abnormal cyanide.}}{\left\{\begin{matrix} C_nH_{2n+1} \\ \mathbf{C}N'''\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Potassic salt.}}{\left\{\begin{matrix} C_nH_{2n+1} \\ \mathbf{C}OKo\end{matrix}\right.} + \underset{\text{Ammonia.}}{\mathbf{N}H_3.}$$

3. The nitriles or abnormal cyanides when submitted to the action of acids yield an ammonic salt and a fatty acid:—

$$\underset{\text{Nitrile.}}{\left\{\begin{matrix} \mathbf{C}_nH_{2n+1} \\ \mathbf{C}N'''\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Ammonic chloride.}}{\mathbf{N}H_4Cl} + \underset{\text{Fatty acid.}}{\left\{\begin{matrix} \mathbf{C}_nH_{2n+1} \\ \mathbf{C}OHo\end{matrix}\right.}.$$

4. The normal cyanides when acted on by acids behave like hydrocyanic acid (see p. 30), producing formic acid and the hydrochlorate of an amine:—

$$\underset{\text{Cyanide.}}{\left\{\begin{matrix} C_nH_{2n+1} \\ \mathbf{N}C\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Formic acid.}}{\left\{\begin{matrix} H \\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Hydrochlorate of amine.}}{\mathbf{N}(C_nH_{2n+1})H_3Cl.}$$

This reaction appears to take place in three stages; and in the case of phenylic cyanide the intermediate compounds have been obtained:—

$$\underset{\text{Phenylic cyanide.}}{2\left\{\begin{matrix}\mathbf{C}_6H_5\\ \mathbf{N}C\end{matrix}\right.} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Formic acid.}}{\left\{\begin{matrix}H\\ \mathbf{CO}Ho\end{matrix}\right.} + \underset{\text{Formyl-diphenyl-diamine.}}{\mathbf{N}_2(CH)'''(C_6H_5)_2H.}$$

$$\underset{\text{Formyl-diphenyl-diamine.}}{\mathbf{N}_2(CH)'''(C_6H_5)_2H} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Phenyl formamide.}}{\left\{\begin{matrix}\mathbf{C}_6H_5\\ \mathbf{N}(COH)H\end{matrix}\right.} + \underset{\text{Phenylamine.}}{\left\{\begin{matrix}\mathbf{C}_6H_5\\ \mathbf{N}H_2\end{matrix}\right.}.$$

$$\underset{\text{Phenyl formamide.}}{\left\{\begin{matrix}\mathbf{C}_6H_5\\ \mathbf{N}(COH)H\end{matrix}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Phenylamine.}}{\left\{\begin{matrix}\mathbf{C}_6H_5\\ \mathbf{N}H_2\end{matrix}\right.} + \underset{\text{Formic acid.}}{\left\{\begin{matrix}H\\ \mathbf{CO}Ho\end{matrix}\right.}.$$

5. When the iodides are digested with zinc or magnesium, the radicals are either liberated or unite with the metal:—

$$\underset{\text{Iodide.}}{2C_nH_{2n+1}I} + 2Zn = \underset{\text{Organo-zinc compound.}}{\mathbf{Zn}(C_nH_{2n+1})_2} + \underset{\text{Zincic iodide.}}{\mathbf{Zn}I_2.}$$

or

$$\underset{\text{Iodide.}}{2C_nH_{2n+1}I} + Zn = \underset{\text{Free radical.}}{\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}_nH_{2n+1}\end{matrix}\right.} + \underset{\text{Zincic iodide.}}{\mathbf{Zn}I_2.}$$

6. When the iodides are submitted to the action of sodic ethylate, a mixed ether (or a simple ether if $n=2$) is formed:—

$$\underset{\text{Sodic ethylate.}}{\mathbf{C}_2H_5Nao} + \underset{\text{Iodide.}}{C_nH_{2n+1}I} = \underset{\text{Ether.}}{\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ O\\ \mathbf{C}_2H_5\end{matrix}\right.} + NaI.$$

7. The haloid ethers of the monad positive radicals are the representatives of the hydracids of mineral chemistry, and unite directly with ammonia, producing salts which, when treated with potassic hydrate, yield compound ammonias containing the positive radical of the haloid ether in the place of one atom of hydrogen:—

$$\underset{\text{Ammonia.}}{\mathbf{N}H_3} + \underset{\text{Ethylic iodide.}}{EtI} = \underset{\text{Ethylammonic iodide.}}{\mathbf{N}H_3EtI.}$$

$$\underset{\text{Ethylammonic iodide.}}{\mathbf{N}H_3EtI} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Ethylamine.}}{\mathbf{N}EtH_2} + \underset{\text{Potassic iodide.}}{KI} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

METHYLIC CHLORIDE.

$\mathbf{C}H_3Cl$ or MeCl.

Molecular weight = 50·5. *Molecular volume* ☐☐. 1 *litre of methylic chloride vapour weighs* 25·25 *criths. Boils at* − 21°.

Preparation.—By heating together sodic chloride, methylic alcohol, and sulphuric acid:—

$$\underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} + \underset{\text{Methylic alcohol.}}{MeHo} = \underset{\text{Sulphomethylic acid.}}{\mathbf{S}O_2MeoHo} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

$$\underset{\text{Sulphomethylic acid.}}{\mathbf{S}O_2MeoHo} + \underset{\text{Sodic chloride.}}{NaCl} = \underset{\text{Methylic chloride.}}{MeCl} + \underset{\text{Hydric sodic sulphate.}}{\mathbf{S}O_2HoNao}.$$

Reaction.—By the action of chlorine, methylic chloride produces three substitution derivatives:—

				Boiling-point.
Monochlorinated	methylic	chloride,	$\mathbf{C}H_2Cl_2$.	31°
Dichlorinated	,,	,,	$\mathbf{C}HCl_3$.	60·8
Trichlorinated	,,	,,	$\mathbf{C}Cl_4$.	78

Chloroform, acted on by powdered zinc and a solution of ammonia, produces methylenic dichloride, boiling between 40° and 42°.

CHLOROFORM, *Dichlorinated Methylic Chloride.*

$\mathbf{C}HCl_3$.

Molecular weight = 119·5. *Molecular volume* ☐☐. 1 *litre of chloroform vapour weighs* 59·75 *criths. Sp. gr. at* 0° 1·525. *Boils at* 61°·2.

Preparation.—This compound is manufactured in large quantities by heating alcohol with a solution of calcic chloro-hypochlorite (*chloride of lime*). It may also be made by treating methylic alcohol in the same manner. For the reaction see p. 83.

Reactions.—1. Chloroform is transformed into potassic formate by boiling with alcoholic potash:—

$$\underset{\text{Chloroform.}}{\mathbf{C}HCl_3} + \underset{\text{Potassic hydrate.}}{4KHo} = \underset{\text{Potassic formate.}}{\mathbf{C}HOKo} + \underset{\text{Potassic chloride.}}{3KCl} + \underset{\text{Water.}}{2\mathbf{O}H_2}.$$

2. When acted upon by chlorine in the presence of sunlight, the hydrogen of chloroform is displaced by chlorine, and carbonic tetrachloride ($\mathbf{C}Cl_4$) formed.

ETHYLIC CHLORIDE.

$\mathbf{C}_2H_5Cl$ or EtCl.

Molecular weight = 64·5. *Molecular volume* ☐☐. 1 *litre of ethylic chloride vapour weighs* 32·25 *criths.* *Sp. gr.* 0·917. *Boils at* 11°·5.

Preparation.—Ethylic alcohol is saturated with hydrochloric acid, and digested in sealed tubes at 100° for one or two hours, when the mixture separates into two layers, the upper one being the ethylic chloride:—

$$\underset{\text{Alcohol.}}{EtHo} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ethylic chloride.}}{EtCl} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

ETHYLIC IODIDE.

$\mathbf{C}_2H_5I$ or EtI.

Molecular weight = 156. *Molecular volume* ☐☐. 1 *litre of ethylic iodide vapour weighs* 78 *criths.* *Sp. gr.* 1·9464. *Boils at* 72°·2.

Preparation.—By placing in a retort two parts by weight of alcohol and one of amorphous phosphorus, and then introducing five parts of iodine and distilling in a water-bath:—

$$\underset{\text{Alcohol.}}{3\mathbf{C}_2H_5Ho} + P + I_3 = \underset{\text{Ethylic iodide.}}{3\mathbf{C}_2H_5I} + \underset{\text{Phosphorous acid.}}{\mathbf{P}OHHo_2}.$$

Reaction.—1. Ethylic iodide, when heated with water in a sealed tube, produces ether and hydriodic acid:—

$$\underset{\text{Ethylic iodide.}}{2\mathbf{C}_2H_5I} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Ether.}}{\left\{\begin{matrix}\mathbf{C}_2H_5\\ O\\ \mathbf{C}_2H_5\end{matrix}\right.} + \underset{\text{Hydriodic acid.}}{2HI}.$$

2. By heating ethylic iodide with argentic nitrite, nitroethane is formed:—

$$\underset{\text{Ethylic iodide.}}{\mathbf{C}_2H_5I} + \underset{\text{Argentic nitrite.}}{\mathbf{N}OAgo} = \underset{\text{Nitroethane.}}{\mathbf{N}(C_2H_5)O_2} + \underset{\text{Argentic iodide.}}{AgI}.$$

3. Heated with potassic sulphite, ethylic iodide yields potassic ethylsulphonate:—

$$\underset{\text{Ethylic iodide.}}{\mathbf{C}_2H_5I} + \underset{\text{Potassic sulphite.}}{\mathbf{S}OKo_2} = \underset{\text{Potassic ethylsulphonate.}}{\left\{\begin{matrix}\mathbf{C}_2H_5\\ \mathbf{S}O_2Ko\end{matrix}\right.} + \underset{\text{Potassic iodide.}}{KI}.$$

The methylic and amylic iodides are similar liquids, and obtained by analogous processes; methylic iodide, $\mathbf{C}H_3I$, has the sp. gr. 2·237, and boils at 44° C. Amylic iodide, $\mathbf{C}_5H_{11}I$, has the sp. gr. 1·511, and boils at 146°.

Analogous compounds of the allyl series have been prepared. Allylic iodide, AllI, is a liquid boiling at 101°. The haloid ethers of the phenyl series have already been described (p. 65).

HALOID ETHERS OF THE DYAD POSITIVE RADICALS.

I. *Haloid ethers of the form* $C_nH_{2n}HoCl$.

Preparation.—These ethers are prepared by the action of the hydracids on the glycols. The following will serve as examples of this class:—

Ethylenic chlorhydrate or chlorhydric glycol $\left\{\begin{matrix}CH_2Ho\\CH_2Cl\end{matrix}\right.$.

Ethylenic iodhydrate or iodhydric glycol.... $\left\{\begin{matrix}CH_2Ho\\CH_2I\end{matrix}\right.$.

Treated with potassic hydrate, both these bodies give ethylenic oxide, as previously described (p. 118).

II. *Haloid ethers of the form* $C_nH_{2n}Cl_2$.

Preparation.—These ethers are generally formed by the direct union of the dyad radicals with the negative elements.

The following list comprises the chief members of this class:—

		Boiling-point.
Methylenic chloride	CH_2Cl_2	40°
,, iodide	CH_2I_2	181
Ethylenic chloride	$C_2H_4Cl_2$	85
,, bromide	$C_2H_4Br_2$	131
,, iodide	$C_2H_4I_2$	—
Propylenic chloride	$C_3H_6Cl_2$	97
,, bromide	$C_3H_6Br_2$	141·6
,, iodide	$C_3H_6I_2$	—
Butylenic chloride	$C_4H_8Cl_2$	127
,, bromide	$C_4H_8Br_2$	160
Amylenic chloride	$C_5H_{10}Cl_2$	—
,, bromide	$C_5H_{10}Br_2$	175

By the action of potassium, sodium, or zinc, the radicals are again liberated, except in the case of the methylene compounds. The bromides are the most important members of the series. Among the higher members numerous isomers are possible, many of which have been prepared.

ETHYLENIC BROMIDE.

$$\mathbf{C}_2H_4Br_2 \text{ or } \left\{\begin{matrix}\mathbf{C}H_2Br\\ \mathbf{C}H_2Br\end{matrix}\right. \text{or } Et''Br_2.$$

Molecular weight = 188. *Molecular volume* □□. 1 *litre of ethylenic bromide vapour weighs* 94 *criths. Sp. gr.* 2·16. *Fuses at* −9°. *Boils at* 131°.

Preparation.—By agitating bromine and water with ethylene.

Reactions.—1. Boiled with alcoholic potash it yields bromethylene or vinylic bromide :—

$$\underset{\substack{\text{Ethylenic}\\ \text{bromide.}}}{\mathbf{C}_2H_4Br_2} + \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{KHo} = \underset{\substack{\text{Vinylic bromide}\\ \text{or bromethylene.}}}{\mathbf{C}_2H_3Br} + \underset{\substack{\text{Potassic}\\ \text{bromide.}}}{KBr} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

2. Heated with an alcoholic solution of potassic acetate, it yields monacetic glycol.

$$\underset{\substack{\text{Ethylenic}\\ \text{bromide.}}}{\left\{\begin{matrix}\mathbf{C}H_2Br\\ \mathbf{C}H_2Br\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\ \text{acetate.}}}{2\mathbf{C}MeOKo} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Monacetic glycol.}}{\left\{\begin{matrix}\mathbf{C}H_2\text{-}\mathbf{O}\text{-}\mathbf{C}MeO\\ \mathbf{C}H_2Ho\end{matrix}\right.}$$

$$+ \underset{\substack{\text{Acetic}\\ \text{acid.}}}{\mathbf{C}MeOHo} = \underset{\substack{\text{Potassic}\\ \text{bromide.}}}{2KBr}.$$

ETHYLENIC CYANIDE, *Succinonitrile.*

$$\left\{\begin{matrix}\mathbf{C}H_2Cy\\ \mathbf{C}H_2Cy\end{matrix}\right. = \mathbf{C}_2H_4Cy_2.$$

Fuses at 37°.

Preparation.—By heating ethylenic bromide with potassic cyanide to 100° for sixteen hours.

$$\underset{\substack{\text{Ethylenic}\\ \text{bromide.}}}{\left\{\begin{matrix}\mathbf{C}H_2Br\\ \mathbf{C}H_2Br\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\ \text{cyanide.}}}{2\mathbf{C}N'''K} = \underset{\substack{\text{Succino-}\\ \text{nitrile.}}}{\left\{\begin{matrix}\mathbf{C}H_2(\mathbf{C}N''')\\ \mathbf{C}H_2(\mathbf{C}N''')\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\ \text{bromide.}}}{2KBr}.$$

Reaction.—When boiled with alcoholic potash, succinonitrile or abnormal ethylenic cyanide yields potassic s cinate:—

$$\underset{\text{Succino-nitrile.}}{\left\{\begin{array}{l}CH_2(CN''')\\CH_2(CN''')\end{array}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Potassic succinate.}}{\left\{\begin{array}{l}CH_2(COKo)\\CH_2(COKo)\end{array}\right.} + \underset{\text{Ammo}}{2N}$$

HALOID ETHERS OF THE TRIAD POSITIVE RADICALS.

I. Of the form $C_nH_{2n-1}Ho_2Cl$.

		Boiling-point.
α-Chlorhydrin ..	$\left\{\begin{array}{l}CH_2Ho\\CHHo\\CH_2Cl\end{array}\right.$	227°
β-Chlorhydrin ..	$\left\{\begin{array}{l}CH_2Ho\\CHCl\\CH_2Ho\end{array}\right.$	230—235
α-Bromhydrin ..	$\left\{\begin{array}{l}CH_2Ho\\CHHo\\CH_2Br\end{array}\right.$	180 *in vacuo.*

II. Of the form $C_nH_{2n-1}HoCl_2$.

α-Dichlorhydrin	$\left\{\begin{array}{l}CH_2Cl\\CHHo\\CH_2Cl\end{array}\right.$	174
β-Dichlorhydrin	$\left\{\begin{array}{l}CH_2Ho\\CHCl\\CH_2Cl\end{array}\right.$	182

III. Of the form $C_nH_{2n-1}Cl_3$.

Trichlorhydrin..	$\left\{\begin{array}{l}CH_2Cl\\CHCl\\CH_2Cl\end{array}\right.$	158

IV. Of the form $C_nH_{2n-1}OCl$.

Hydrochloric glycide or epichlorhydrin ..	$\left\{\begin{array}{l}\left.\begin{array}{l}CH_2\\CH\end{array}\right.O\\CH_2Cl\end{array}\right.$	118

Preparation.—The ethers of the first three forms are obtained by the action of the hydracids upon glycerin; whilst those of the fourth are produced by the action of alkalies upon the second form of compounds. β-Chlorhydrin is obtained by the direct union of hypochlorous acid with allylic alcohol, β-dichlorhydrin by the direct union of chlorine with allylic alcohol.

CHAPTER XV.

THE ALDEHYDES.

THESE compounds are intermediate between the alcohols and the acids. They are formed from alcohols by the abstraction of hydrogen; hence the name, which is an abbreviation of *alcohol dehydrogenatum*.

Three series of aldehydes are known, corresponding to the three series of monacid alcohols, viz.:—

A. Aldehydes derived from $C_nH_{2n+1}Ho$ alcohols.
B. " " " $C_nH_{2n-1}Ho$ "
C. " " " $C_nH_{2n-7}Ho$ "

Preparation.—1. The aldehydes are formed by the oxidation of the alcohols; ethylic alcohol, for instance, yields acetic aldehyde:—

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{array}{l}CH_3\\ CH_2Ho\end{array}\right.} + O = \underset{\text{Acetic aldehyde*.}}{\left\{\begin{array}{l}CH_3\\ COH\end{array}\right.} + \underset{\text{Water.}}{OH_2.}$$

2. Aldehydes are also formed by distilling a mixture of

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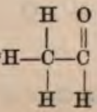


$$\begin{array}{ccccc} & & H & & O \\ & & | & & \| \\ H & - & C & - & C \\ & & | & & | \\ & & H & & H \end{array}$$

molecular quantities of the potassic salt of a fatty acid and of potassic formate:—

$$\underset{\text{Potassic acetate.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COKo}\end{array}\right.} + \underset{\text{Potassic formate.}}{\left\{\begin{array}{l}\mathrm{H}\\ \mathrm{COKo}\end{array}\right.} = \underset{\text{Acetic aldehyde.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COH}\end{array}\right.} + \underset{\text{Potassic carbonate.}}{\mathrm{COKo_2}}.$$

This is an important reaction, as by its means the series of fatty acids can be ascended; for the aldehyde may next be transformed into an alcohol by nascent hydrogen, then the alcohol converted into an abnormal cyanide or nitrile, which by treatment with potassic hydrate gives the potassic salt of the next higher acid. Thus:—

$$\underset{\text{Acetic aldehyde.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COH}\end{array}\right.} + \mathrm{H_2} = \underset{\text{Ethylic alcohol.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2Ho}\end{array}\right.};$$

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2Ho}\end{array}\right.} + \underset{\text{Sulphuric acid.}}{\mathrm{SO_2Ho_2}} = \underset{\text{Sulphovinic acid.}}{\mathrm{SO_2HoEto}} + \underset{\text{Water.}}{\mathrm{OH_2}};$$

$$\underset{\text{Potassic sulphovinate.}}{\mathrm{SO_2KoEto}} + \underset{\text{Potassic cyanide.}}{\mathrm{CN'''K}} = \underset{\text{Potassic sulphate.}}{\mathrm{SO_2Ko_2}} + \underset{\text{Propionitrile.}}{\left\{\begin{array}{l}\mathrm{CMeH_2}\\ \mathrm{CN'''}\end{array}\right.};$$

$$\underset{\text{Propionitrile.}}{\left\{\begin{array}{l}\mathrm{CMeH_2}\\ \mathrm{CN'''}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{\mathrm{KHo}} + \underset{\text{Water.}}{\mathrm{OH_2}} = \underset{\text{Potassic propionate.}}{\left\{\begin{array}{l}\mathrm{CMeH_2}\\ \mathrm{COKo}\end{array}\right.} + \underset{\text{Ammonia.}}{\mathrm{NH_3}}.$$

Starting again with potassic propionate instead of potassic acetate, the same series of reactions can be performed, resulting in potassic butyrate, and so on.

Reactions.—1. By direct absorption of oxygen, the aldehydes are transformed into the corresponding acids:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{array}{l}\mathrm{C_nH_{2n+1}}\\ \mathrm{COH}\end{array}\right.} + \mathrm{O} = \underset{\text{Acid.}}{\left\{\begin{array}{l}\mathrm{C_nH_{2n+1}}\\ \mathrm{COHo}\end{array}\right.}.$$

2. Also heated with ammoniacal solution of argentic oxide,

the aldehydes are converted into acids, metallic silver being deposited:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{matrix}\mathrm{C_nH_{2n+1}}\\ \mathrm{COH}\end{matrix}\right.} + \underset{\text{Argentic oxide.}}{\mathrm{OAg_2}} = \underset{\text{Acid.}}{\left\{\begin{matrix}\mathrm{C_nH_{2n+1}}\\ \mathrm{COHo}\end{matrix}\right.} + \mathrm{Ag_2}.$$

3. When heated with potassic hydrate, the aldehydes yield the potassic salts of the corresponding acids, with evolution of hydrogen:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{matrix}\mathrm{C_nH_{2n+1}}\\ \mathrm{COH}\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{\mathrm{KHo}} = \underset{\substack{\text{Potassic}\\ \text{salt.}}}{\left\{\begin{matrix}\mathrm{C_nH_{2n+1}}\\ \mathrm{COKo}\end{matrix}\right.} + \mathrm{H_2}.$$

4. Treated with nascent hydrogen, they are converted into the corresponding alcohols:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{matrix}\mathrm{C_nH_{2n+1}}\\ \mathrm{COH}\end{matrix}\right.} + \mathrm{H_2} = \underset{\text{Alcohol.}}{\left\{\begin{matrix}\mathrm{C_nH_{2n+1}}\\ \mathrm{CH_2Ho}\end{matrix}\right.}.$$

5. Most aldehydes combine directly with ammonia, forming crystalline compounds:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{matrix}\mathrm{C_nH_{2n+1}}\\ \mathrm{COH}\end{matrix}\right.} + \underset{\text{Ammonia.}}{\mathrm{NH_3}} = \underset{\substack{\text{Ammonium}\\ \text{compound.}}}{\left\{\begin{matrix}\mathrm{C_nH_{2n+1}}\\ \mathrm{CH(NH_2)Ho}\end{matrix}\right.}.$$

6. Aldehydes also combine with the alkaline hydric sulphites, producing crystalline compounds:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{matrix}\mathrm{C_nH_{2n+1}}\\ \mathrm{COH}\end{matrix}\right.} + \underset{\substack{\text{Hydric potassic}\\ \text{sulphite.}}}{\mathrm{SOKoHo}} = \left\{\begin{matrix}\mathrm{C_nH_{2n+1}}\\ \mathrm{CH(O\text{-}SOKo)Ho}\end{matrix}\right..$$

A. *ALDEHYDES DERIVED FROM THE* $\mathrm{C_nH_{2n+1}Ho}$ *SERIES OF ALCOHOLS.*

The following are known:—

		Fusing-point.	Boiling-point.
Formic aldehyde...	$\left\{\begin{matrix}\mathrm{H}\\ \mathrm{COH}\end{matrix}\right.$	—	—

		Fusing-point.	Boiling-point.
Acetic aldehyde	$\left\{\begin{matrix} CH_3 \\ COH \end{matrix}\right.$	—	21°
Propionic aldehyde	$\left\{\begin{matrix} CMeH_2 \\ COH \end{matrix}\right.$ or $\left\{\begin{matrix} C(CH_3)H_2 \\ COH \end{matrix}\right.$	—	48·7
Butyric aldehyde	$\left\{\begin{matrix} CEtH_2 \\ COH \end{matrix}\right.$ or $\left\{\begin{matrix} C(C_2H_5)H_2 \\ COH \end{matrix}\right.$	—	75
Valeric aldehyde	$\left\{\begin{matrix} CPrH_2 \\ COH \end{matrix}\right.$ or $\left\{\begin{matrix} C(C_3H_7)H_2 \\ COH \end{matrix}\right.$	—	93
Œnanthic aldehyde.	$\left\{\begin{matrix} CAyH_2 \\ COH \end{matrix}\right.$ or $\left\{\begin{matrix} C(C_5H_{11})H_2 \\ COH \end{matrix}\right.$	below −12°	154
Capric aldehyde	$\left\{\begin{matrix} C(C_8H_{17})H_2 \\ COH \end{matrix}\right.$	− 2	228?
Euodic aldehyde	$\left\{\begin{matrix} C(C_9H_{19})H_2 \\ COH \end{matrix}\right.$	+ 7	213
Lauric aldehyde	$\left\{\begin{matrix} C(C_{10}H_{21})H_2 \\ COH \end{matrix}\right.$	44·5	—
Myristic aldehyde	$\left\{\begin{matrix} C(C_{12}H_{25})H_2 \\ COH \end{matrix}\right.$	52·5	—
Palmitic aldehyde	$\left\{\begin{matrix} C(C_{14}H_{29})H_2 \\ COH \end{matrix}\right.$	58·5	—
Stearic aldehyde	$\left\{\begin{matrix} C(C_{16}H_{33})H_2 \\ COH \end{matrix}\right.$	63·5	—

ACETIC ALDEHYDE, *Aldehyde.*

$$\left\{\begin{matrix} CH_3 \\ COH \end{matrix}\right.\cdot$$

Molecular weight = 44. *Molecular volume* □□· 1 *litre of aldehyde vapour weighs* 22 *criths. Sp. gr.* = 0·807. *Boils at* 21°.

Preparation.—1. By oxidising alcohol with chromic acid, chlorine water, or manganic oxide and sulphuric acid.

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix} CH_3 \\ CH_2Ho \end{matrix}\right.} + O = \underset{\text{Acetic aldehyde.}}{\left\{\begin{matrix} CH_3 \\ COH \end{matrix}\right.} + \underset{\text{Water.}}{OH_2}.$$

2. By oxidation, casein, fibrin, and albumen also yield aldehyde.

3. Aldehyde is formed when the vapour of alcohol or ether is passed through a tube heated to dull redness.

Reactions.—1. It gradually absorbs oxygen from the air, forming acetic acid, into which it is also readily converted by oxidizing agents:—

$$\underset{\text{Acetic aldehyde.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COH}\end{array}\right.} + \mathrm{O} = \underset{\text{Acetic acid.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COHo}\end{array}\right.}$$

2. It reduces silver salts, depositing lustrous metallic silver on the sides of the vessel.

3. By the action of phosphoric chloride on aldehyde, ethylidenic dichloride is produced:—

$$\underset{\text{Acetic aldehyde.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COH}\end{array}\right.} + \underset{\text{Phosphoric chloride.}}{\mathrm{PCl_5}} = \underset{\text{Ethylidenic dichloride.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CHCl_2}\end{array}\right.} + \underset{\text{Phosphoric oxytrichloride.}}{\mathrm{POCl_3}}.$$

4. When submitted to the action of potassium, one atom of hydrogen is substituted by an atom of the metal, the compound

$$\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COK}\end{array}\right.$$

being formed.

5. Hydrocyanic acid transforms aldehyde into alanin:—

$$\underset{\text{Acetic aldehyde.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COH}\end{array}\right.} + \underset{\text{Hydrocyanic acid.}}{\mathrm{NCH}} + \underset{\text{Water.}}{\mathrm{OH_2}} = \underset{\text{Alanin.}}{\left\{\begin{array}{l}\mathrm{CMeH(N'''H_2)}.\\ \mathrm{COHo}\end{array}\right.}$$

By the action of nitrous anhydride, alanin or lactamic acid s converted into lactic acid:—

$$2\underset{\text{Alanin.}}{\left\{\begin{array}{l}\mathrm{CMeH(N'''H_2)}\\ \mathrm{COHo}\end{array}\right.} + \underset{\text{Nitrous anhydride.}}{\mathrm{N_2O_3}} = 2\underset{\text{Lactic acid.}}{\left\{\begin{array}{l}\mathrm{CMeHHo}\\ \mathrm{COHo}\end{array}\right.} + 2\mathrm{N_2} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

There are two isomeric modifications of aldehyde:—

Metaldehyde, crystalline, subliming at 120°.
Paraldehyde, liquid, boiling at 125°.

By the action of chlorine upon alcohol, trichloraldehyde is formed containing 3 atoms of chlorine in the place of 3 atoms of methylic hydrogen. It is named *chloral*:—

$$\left\{\begin{array}{l}\mathbf{C}Cl_3\\ \mathbf{C}OH\end{array}\right.\cdot$$

This compound immediately unites with one molecule of water, forming *chloral hydrate*, which has the following constitutional formula:—

$$\left\{\begin{array}{l}\mathbf{C}Cl_3\\ \mathbf{C}HHo_2\end{array}\right.\cdot$$

In the same operation *chloral alcoholate* is generally produced. Its constitution is expressed by the following formula:—

$$\left\{\begin{array}{l}\mathbf{C}Cl_3\\ \mathbf{C}HEtoHo\end{array}\right.\cdot$$

B. *ALDEHYDES DERIVED FROM THE* $C_nH_{2n+1}Ho$ *ALCOHOLS.*

		Boiling-point.
Acrolein (acrylic aldehyde)......	$\left\{\begin{array}{l}\mathbf{C}Me''H\\ \mathbf{C}OH\end{array}\right.$	52·4°
Crotonic aldehyde "	$\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H\\ \mathbf{C}H\\ \mathbf{C}OH\end{array}\right.$	104—105

ACROLEIN, *Acrylic Aldehyde.*

$$\left\{\begin{array}{l}\mathbf{C}Me''H\\ \mathbf{C}OH\end{array}\right.\cdot$$

Molecular weight = 56. *Molecular volume* $\square\!\square$. 1 *litre of acrolein vapour weighs* 28 *criths. Boils at* 52°·4.

Preparation.—1. By the action of phosphoric anhydride or of sulphuric acid on glycerin:—

$$\underset{\text{Glycerin.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\\ \mathbf{C}H_2Ho\end{array}\right.} = \underset{\text{Water.}}{2\mathbf{O}H_2} + \underset{\text{Acrolein.}}{\left\{\begin{array}{l}\mathbf{C}Me''H\\ \mathbf{C}OH\end{array}\right.}\cdot$$

2. By the oxidation of allylic alcohol :—

$$\underset{\text{Allylic alcohol}}{\left\{\begin{matrix}\mathrm{CMe''H}\\ \mathrm{CH_2Ho}\end{matrix}\right.} + \mathrm{O} + \underset{\text{Acrolein.}}{\left\{\begin{matrix}\mathrm{CMe''H}\\ \mathrm{COH}\end{matrix}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

3. By the action of heat on the product of the union of acetone with bromine :—

$$\underset{\text{Acetone.}}{\left\{\begin{matrix}\mathrm{COMe}\\ \mathrm{CH_3}\end{matrix}\right.} + \mathrm{Br_2} = \left\{\begin{matrix}\mathrm{CMeBr_2}\\ \mathrm{CH_2Ho}\end{matrix}\right. :$$

$$\left\{\begin{matrix}\mathrm{CMeBr_2}\\ \mathrm{CH_2Ho}\end{matrix}\right. = \underset{\text{Acrolein.}}{\left\{\begin{matrix}\mathrm{CMe''H}\\ \mathrm{COH}\end{matrix}\right.} + \underset{\text{Hydrobromic acid.}}{\mathrm{2HBr}}.$$

Reaction.—By oxidation, acrolein yields acrylic acid :—

$$\underset{\text{Acrolein.}}{\left\{\begin{matrix}\mathrm{CMe''H}\\ \mathrm{COH}\end{matrix}\right.} + \mathrm{O} = \underset{\text{Acrylic acid.}}{\left\{\begin{matrix}\mathrm{CMe''H}\\ \mathrm{COHo}\end{matrix}\right.} .$$

C. *ALDEHYDES DERIVED FROM THE* $C_nH_{2n-7}Ho$ *ALCOHOLS.*

		Boiling-point.
Benzoic aldehyde.....	$\left\{\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{COH}\end{matrix}\right.$	180°
Metatoluic aldehyde ..	$\left\{\begin{matrix}\mathrm{C_6H_4Me}\\ \mathrm{COH}\end{matrix}\right.$ (1 : 3) ..	199
Paratoluic aldehyde ..	$\left\{\begin{matrix}\mathrm{C_6H_4Me}\\ \mathrm{COH}\end{matrix}\right.$ (1 : 4) ..	204
Phenylacetic aldehyde	$\left\{\begin{matrix}\mathrm{CPhH_2}\\ \mathrm{COH}\end{matrix}\right.$	205—207
Cuminic aldehyde	$\left\{\begin{matrix}\mathrm{C_6H_4\beta Pr}\\ \mathrm{COH}\end{matrix}\right.$ (1 : 4)..	237

BENZOIC ALDEHYDE, *Oil of Bitter Almonds, Hydride of Benzoyl.*

$$\left\{\begin{matrix}\mathbf{C}_6\mathrm{H}_5\\ \mathbf{C}\mathrm{OH}\end{matrix}\right.\cdot$$

Molecular weight = 106. *Molecular volume* ☐☐· 1 *litre of benzoic aldehyde vapour weighs* 53 *criths.* *Sp. gr. at* 15° = 1·0504. *Boils at* 180°.

Preparation.—1. By the oxidation of amygdalin by nitric acid, and by the action of a mixture of manganic oxide and sulphuric acid on albumen, fibrin, casein, and gelatin.

2. By digesting bitter almonds with water for five or six hours at 30°—40°. The synaptase present acts as a ferment on the amygdalin, converting it into glucose, benzoic aldehyde, and hydrocyanic acid:—

$$\underset{\text{Amygdalin.}}{\mathrm{C}_{20}\mathrm{H}_{27}\mathrm{NO}_{11}} + \underset{\text{Water.}}{2\mathbf{O}\mathrm{H}_2} = \underset{\substack{\text{Benzoic}\\ \text{aldehyde.}}}{\left\{\begin{matrix}\mathbf{C}_6\mathrm{H}_5\\ \mathbf{C}\mathrm{OH}\end{matrix}\right.} + \underset{\substack{\text{Hydrocyanic}\\ \text{acid.}}}{\mathbf{N}\mathrm{CH}} + \underset{\text{Glucose.}}{2\mathrm{C}_6\mathrm{H}_{12}\mathrm{O}_6}.$$

3. By digesting together plumbic nitrate, water, and benzylic chloride, benzoic aldehyde is formed:—

$$2\underset{\substack{\text{Benzylic}\\ \text{chloride.}}}{\left\{\begin{matrix}\mathbf{C}_6\mathrm{H}_5\\ \mathbf{C}\mathrm{H}_2\mathrm{Cl}\end{matrix}\right.} + \underset{\substack{\text{Plumbic}\\ \text{nitrate.}}}{\mathbf{N}_2\mathrm{O}_4\mathrm{Pbo}''} = \underset{\substack{\text{Nitrous}\\ \text{anhydride.}}}{\mathbf{N}_2\mathrm{O}_3} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2} + \underset{\substack{\text{Plumbic}\\ \text{chloride.}}}{\mathbf{Pb}\mathrm{Cl}_2} + 2\underset{\substack{\text{Benzoic}\\ \text{aldehyde.}}}{\left\{\begin{matrix}\mathbf{C}_6\mathrm{H}_5\\ \mathbf{C}\mathrm{OH}\end{matrix}\right.}\cdot$$

The benzylic chloride is prepared by passing chlorine into the vapour of boiling toluol.

Reactions.—1. When exposed to the air, benzoic aldehyde absorbs oxygen and is converted into benzoic acid:—

$$\underset{\text{Benzoic aldehyde.}}{\left\{\begin{matrix}\mathbf{C}_6\mathrm{H}_5\\ \mathbf{C}\mathrm{OH}\end{matrix}\right.} + \mathrm{O} = \underset{\text{Benzoic acid.}}{\left\{\begin{matrix}\mathbf{C}_6\mathrm{H}_5\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right.}\cdot$$

2. Heated with solid potassic hydrate, it gives hydrogen and potassic benzoate:—

$$\underset{\substack{\text{Benzoic}\\\text{aldehyde.}}}{\left\{\begin{matrix}\mathbf{C}_6H_5\\\mathbf{C}OH\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\substack{\text{Potassic}\\\text{benzoate.}}}{\left\{\begin{matrix}\mathbf{C}_6H_5\\\mathbf{C}OHo\end{matrix}\right.} + H_2.$$

3. Heated with alcoholic potash, the same reaction takes place, but the hydrogen, instead of being evolved, reduces a second molecule of benzoic aldehyde to benzylic alcohol:—

$$2\underset{\substack{\text{Benzoic}\\\text{aldehyde.}}}{\left\{\begin{matrix}\mathbf{C}_6H_5\\\mathbf{C}OH\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\substack{\text{Potassic}\\\text{benzoate.}}}{\left\{\begin{matrix}\mathbf{C}_6H_5\\\mathbf{C}OKo\end{matrix}\right.} + \underset{\substack{\text{Benzylic}\\\text{alcohol.}}}{\left\{\begin{matrix}\mathbf{C}_6H_5\\\mathbf{C}H_2Ho\end{matrix}\right.}$$

CHAPTER XVI.

THE ACIDS.

THE acids form the most numerous family of organic compounds.

Many of them are contained in plants in the free state, or in combination as metallic or ethereal salts.

Others are produced by the action of chemical agents on various organic substances.

Some are formed in the animal organism, as, for instance, formic, paralactic, oleic, and stearic acids.

The organic acids are divided into three great classes, according to their basicity:—

1. Monobasic acids.
2. Dibasic acids.
3. Tribasic acids.

The basicity of organic acids is determined by the following simple law:—*an organic acid containing* n *semimolecules of oxatyl is* n-*basic*.

MONOBASIC ACIDS.

The monobasic acids, which always contain a single semimolecule of oxatyl ($\mathbf{C}OHo$), include the six following series:—

	General formulæ.
1. Acetic or fatty series	$\left\{\begin{matrix}\mathbf{C}_nH_{2n+1} \\ \mathbf{C}OHo\end{matrix}\right.$.
2. Acrylic or oleic series	$\left\{\begin{matrix}\mathbf{C}(C_nH_{2n})''(C_mH_{2m+1}) \\ \mathbf{C}OHo\end{matrix}\right.$.
3. Lactic series	$\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})(C_mH_{2m+1})Ho \\ \mathbf{C}OHo\end{matrix}\right.$.
4. Pyruvic series	$\left\{\begin{matrix}\mathbf{C}O(C_nH_{2n+1}) \\ \mathbf{C}OHo\end{matrix}\right.$.
5. Glyoxylic series	$\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})Ho_2 \\ \mathbf{C}OHo\end{matrix}\right.$.
6. Benzoic or aromatic series	$\left\{\begin{matrix}\mathbf{C}_nH_{2n-7} \\ \mathbf{C}OHo\end{matrix}\right.$.

The 1st, 2nd, 3rd, 5th, and 6th of these series may be regarded as the derivatives from corresponding series of alcohols.

1. The Acetic series from the Methyl series of alcohols.
2. ,, Acrylic ,, ,, Allyl ,, ,,
3. ,, Lactic ,, ,, Glycol ,, ,,
5. ,, Glyoxylic,, ,, Glycerin ,, ,,
6. ,, Benzoic ,, ,, Phenyl ,, ,,

The acids of the first, second, fourth, and sixth series are termed *monohydric* as well as monobasic; whilst the acids of the third series are termed *dihydric* and monobasic, indicating their origin from the dihydric alcohols, and that they contain two semimolecules of hydroxyl, one of which is in the oxatyl or negative part, and the other in the positive part of the molecule. The hydrogen of the latter hydroxyl may be displaced by highly positive metals, in the same manner as the hydrogen of the hydroxyl in alcohols; but it cannot be displaced by double decomposition with bases, in the same manner as the hydrogen in the oxatyl may be substituted.

The acids of the fifth series are termed *trihydric* and monobasic, indicating that they are derived from the trihydric alcohols, and that they contain, besides the hydroxyl in the oxatyl, two other semimolecules of hydroxyl in the positive *part of* the molecule.

1. *ACETIC OR FATTY SERIES OF ACIDS.*

General formula.. $\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}OHo\end{matrix}\right.$.

These acids may be conveniently arranged under three divisions, viz.:—

A. Normal acids.

General formula.. $\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}OHo\end{matrix}\right.$.

B. Secondary acids.

General formula.. $\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})_2H\\ \mathbf{C}OHo\end{matrix}\right.$.

C. Tertiary acids.

General formula.. $\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})_3\\ \mathbf{C}OHo\end{matrix}\right.$.

A. *NORMAL ACIDS OF THE ACETIC OR FATTY SERIES.*

General formula.. $\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}OHo\end{matrix}\right.$.

In formic acid, which is generally considered to be the first term of this division, the radical $\mathbf{C}(C_nH_{2n+1})H_2$ is replaced by H; and in acetic acid the value of $n = 0$. In reference to the following list of normal fatty acids, it must be borne in mind that the normal character has not been established in the case of those members which possess a higher molecular weight than œnanthylic acid:—

		Fusing-point.	Boiling-point.
Formic acid	$\left\{\begin{matrix}H\\ \mathbf{C}OHo\end{matrix}\right.$	8·6°	99°
Acetic acid	$\left\{\begin{matrix}Me\\ \mathbf{C}OHo\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$	17	118
Propionic acid	$\left\{\begin{matrix}\mathbf{C}MeH_2\\ \mathbf{C}OHo\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(CH_3)H_2\\ \mathbf{C}OHo\end{matrix}\right.$	—	141
Butyric acid	$\left\{\begin{matrix}\mathbf{C}EtH_2\\ \mathbf{C}OHo\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(C_2H_5)H_2\\ \mathbf{C}OHo\end{matrix}\right.$	below −20	163

		Fusing-point.	Boiling-point.
Valeric acid	$\left\{\begin{array}{l} CPrH_2 \\ COHo \end{array}\right.$ or $\left\{\begin{array}{l} C(C_3H_7)H_2 \\ COHo \end{array}\right.$	—	184·5°
Isopropacetic acid	$\left\{\begin{array}{l} C\beta PrH_2 \\ COHo \end{array}\right.$ or $\left\{\begin{array}{l} C(CMe_2H)H_2 \\ COHo \end{array}\right.$	—	175
Caproic acid	$\left\{\begin{array}{l} CBuH_2 \\ COHo \end{array}\right.$ or $\left\{\begin{array}{l} C(C_4H_9)H_2 \\ COHo \end{array}\right.$	− 2	205
Isocaproic acid	$\left\{\begin{array}{l} C\beta BuH_2 \\ COHo \end{array}\right.$ or „	—	199·7
Œnanthylic acid	$\left\{\begin{array}{l} CAyH_2 \\ COHo \end{array}\right.$ or $\left\{\begin{array}{l} C(C_5H_{11})H_2 \\ COHo \end{array}\right.$	−10·5	223·5
Caprylic acid	$\left\{\begin{array}{l} CCpH_2 \\ COHo \end{array}\right.$ or $\left\{\begin{array}{l} C(C_6H_{13})H_2 \\ COHo \end{array}\right.$	+ 14	236
Pelargonic acid	$\left\{\begin{array}{l} C(C_7H_{15})H_2 \\ COHo \end{array}\right.$	12	253·5
Capric acid	$\left\{\begin{array}{l} C(C_8H_{17})H_2 \\ COHo \end{array}\right.$	27·2(30°)	—
Undecylic acid	$\left\{\begin{array}{l} C(C_9H_{19})H_2 \\ COHo \end{array}\right.$	28·5	—
Lauric acid	$\left\{\begin{array}{l} C(C_{10}H_{21})H_2 \\ COHo \end{array}\right.$	43·6	—
Tridecylic acid	$\left\{\begin{array}{l} C(C_{11}H_{23})H_2 \\ COHo \end{array}\right.$	40·5	—
Myristic acid	$\left\{\begin{array}{l} C(C_{12}H_{25})H_2 \\ COHo \end{array}\right.$	53·8	—
Pentadecylic acid	$\left\{\begin{array}{l} C(C_{13}H_{27})H_2 \\ COHo \end{array}\right.$	51	—
Palmitic acid	$\left\{\begin{array}{l} C(C_{14}H_{29})H_2 \\ COHo \end{array}\right.$	62	—
Margaric acid	$\left\{\begin{array}{l} C(C_{15}H_{31})H_2 \\ COHo \end{array}\right.$	59·9	—
Stearic acid	$\left\{\begin{array}{l} C(C_{16}H_{33})H_2 \\ COHo \end{array}\right.$	69·2	—
Arachidic acid	$\left\{\begin{array}{l} C(C_{18}H_{37})H_2 \\ COHo \end{array}\right.$	75	—
Behenic acid	$\left\{\begin{array}{l} C(C_{20}H_{41})H_2 \\ COHo \end{array}\right.$	76	—
Hyænasic acid	$\left\{\begin{array}{l} C(C_{23}H_{47})H_2 \\ COHo \end{array}\right.$	77	—
Cerotic acid	$\left\{\begin{array}{l} C(C_{25}H_{51})H_2 \\ COHo \end{array}\right.$	78	—
Melissic acid	$\left\{\begin{array}{l} C(C_{28}H_{57})H_2 \\ COHo \end{array}\right.$	88	—

Occurrence.—The greater number of the acids of this series are met with already formed in nature, some in the free state, as formic acid in ants and nettles, valeric acid in the valerian root, pelargonic acid in the essential oil of the *Pelargonium roseum*, and cerotic acid in bee's-wax.

Others are met with as the ethereal salts of monohydric alcohols. Thus spermaceti is cetylic palmitate, and chinese wax cerylic cerotate.

A large number exist as natural fats in the form of the ethereal salts of glycerin: this is the case with butyric, palmitic, and stearic acids, which united with glycerin, form respectively butyrin, palmitin, and stearin.

Formation.—1. By the oxidation of the normal alcohols of the methyl series, as in the conversion of alcohol into acetic acid by heating it with a solution of chromic acid:—

$$\begin{array}{ccccccc} \left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{matrix}\right. & + & O_2 & = & \left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right. & + & \mathbf{O}H_2. \\ \text{Alcohol.} & & & & \text{Acetic acid.} & & \text{Water.} \end{array}$$

2. By the action of alkalies or acids upon the nitriles or abnormal cyanides of the C_nH_{2n+1} series of radicals:—

$$\begin{array}{ccccccccc} \left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}N'''\end{matrix}\right. & + & KHo & + & \mathbf{O}H_2 & = & \left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}OKo\end{matrix}\right. & + & \mathbf{N}H_3; \\ \text{Nitrile.} & & \text{Potassic hydrate.} & & \text{Water.} & & \text{Potassic salt.} & & \text{Ammonia.} \end{array}$$

and

$$\begin{array}{ccccccccc} \left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}N'''\end{matrix}\right. & + & HCl & + & 2\mathbf{O}H_2 & = & \left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}OHo\end{matrix}\right. & + & \mathbf{N}H_4Cl. \\ \text{Nitrile.} & & \text{Hydrochloric acid.} & & \text{Water.} & & \text{Acid.} & & \text{Ammonic chloride.} \end{array}$$

Instances of these reactions are seen in the treatment of propionitrile by a boiling solution of potassic hydrate, when it is converted into potassic propionate, ammonia being evolved, thus—

$$\begin{array}{ccccccccc} \left\{\begin{matrix}\mathbf{C}MeH_2\\ \mathbf{C}N'''\end{matrix}\right. & + & KHo & + & \mathbf{O}H_2 & = & \left\{\begin{matrix}\mathbf{C}MeH_2\\ \mathbf{C}OKo\end{matrix}\right. & + & \mathbf{N}H_3; \\ \text{Propionitrile.} & & \text{Potassic hydrate.} & & \text{Water.} & & \text{Potassic propionate.} & & \text{Ammonia.} \end{array}$$

and in the conversion of propionitrile, by the action of hydrochloric acid, into ammonic chloride and propionic acid :—

$$\underset{\text{Propionitrile.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{MeH_2}\\ \mathbf{C}\mathrm{N'''}\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}} + \underset{\text{Water.}}{2\mathbf{O}\mathrm{H_2}} = \underset{\text{Propionic acid.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{MeH_2}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right.} + \underset{\text{Ammonic chloride.}}{\mathbf{N}\mathrm{H_4Cl}}.$$

3. By the action of the potassium or sodium compounds of the C_nH_{2n+1} radicals upon carbonic anhydride—

$$\underset{\text{Carbonic anhydride.}}{\mathbf{C}\mathrm{O_2}} + \underset{\text{Sodium compound.}}{\mathbf{C}_n\mathrm{H}_{2n+1}\mathrm{Na}} = \underset{\text{Sodic salt.}}{\left\{\begin{matrix}\mathbf{C}_n\mathrm{H}_{2n+1}\\ \mathbf{C}\mathrm{ONao}\end{matrix}\right.},$$

as, for example, in the formation of sodic propionate by the absorption of carbonic anhydride by sodic ethide :—

$$\underset{\text{Carbonic anhydride.}}{\mathbf{C}\mathrm{O_2}} + \underset{\text{Sodic ethide.}}{\mathbf{C}\mathrm{MeH_2Na}} = \underset{\text{Sodic propionate.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{MeH_2}\\ \mathbf{C}\mathrm{ONao}\end{matrix}\right.}.$$

4. By the oxidation of aldehydes—

$$\underset{\text{Aldehyde.}}{\left\{\begin{matrix}\mathbf{C}_n\mathrm{H}_{2n+1}\\ \mathbf{C}\mathrm{OH}\end{matrix}\right.} + \mathrm{O} = \underset{\text{Acid.}}{\left\{\begin{matrix}\mathbf{C}_n\mathrm{H}_{2n+1}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right.},$$

as in the conversion of acetic aldehyde into acetic acid by the absorption of atmospheric oxygen—

$$\underset{\text{Acetic aldehyde.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{OH}\end{matrix}\right.} + \mathrm{O} = \underset{\text{Acetic acid.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right.}.$$

Besides these reactions of general application, there are numerous special methods for the production of certain members of this series. In most of these methods, however, the reactions cannot be clearly traced.

Thus, by the oxidation of albumen, fibrin, casein, and other similar substances, there are produced formic, acetic, propionic, butyric, valeric, and caproic acids.

Propionic and butyric acids are produced in some kinds of fermentation; and acetic acid is obtained by the destructive distillation of wood and similar substances.

Relations of the Normal Fatty Acids to the C_nH_{2n+1} *Series of Radicals.*

1. When the salts of these acids are submitted to electrolysis, the metal goes to the negative electrode, whilst the rest of the molecule splits into carbonic anhydride and the positive radical of the acid.

$$\underset{\text{Sodium salt.}}{2\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}ONao\end{matrix}\right.} = \underset{\text{Positive radical.}}{\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}_nH_{2n+1}\end{matrix}\right.} + \underset{\text{Carbonic anhydride.}}{2\mathbf{C}O_2} + Na_2.$$

On electrolyzing a solution of potassic valerate, hydric potassic carbonate and the normal radical butyl are formed:—

$$\underset{\text{Potassic valerate.}}{2\left\{\begin{matrix}\mathbf{C}_4H_9\\ \mathbf{C}OKo\end{matrix}\right.} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Butyl.}}{\left\{\begin{matrix}\mathbf{C}_4H_9\\ \mathbf{C}_4H_9\end{matrix}\right.} + \underset{\text{Hydric potassic carbonate.}}{2\mathbf{C}OHoKo} + H_2.$$

2. When the ammonic salts of these acids are heated with phosphoric anhydride, they are converted into the nitriles or abnormal cyanides of the radicals of the C_nH_{2n+1} series:—

$$\underset{\text{Ammonic salt.}}{\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}O(N^vH_4O)\end{matrix}\right.} + \underset{\text{Phosphoric anhydride.}}{2\mathbf{P}_2O_5} = \underset{\text{Nitrile.}}{\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}N'''\end{matrix}\right.} + \underset{\text{Metaphosphoric acid.}}{4\mathbf{P}O_2Ho},$$

as in the transformation of ammonic acetate into acetonitrile by distillation with phosphoric anhydride:—

$$\underset{\text{Ammonic acetate.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}O(N^vH_4O)\end{matrix}\right.} + \underset{\text{Phosphoric anhydride.}}{2\mathbf{P}_2O_5} = \underset{\text{Aceto-nitrile.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}N'''\end{matrix}\right.} + \underset{\text{Metaphosphoric acid.}}{4\mathbf{P}O_2Ho}.$$

These abnormal cyanides are converted into monohydric alcohols by Mendius's reaction (see p. 81).

From the alcohols so obtained, the C_nH_{2n+1} radicals are isolated as described at page 79.

Relations of the Normal Fatty Acids to the $C_nH_{2n+1}Ho$ *Series of Alcohols.*

1. By oxidation the normal alcohols yield these acids, as above shown.

2. Conversely, the normal fatty acids can be converted into the C_nH_{2n+1} Ho alcohols,—

1st, by Mendius's reaction (see p. 81);

2nd, by Piria and Wurtz's reactions, viz.:—

Distillation of the potassic salt of the fatty acid with an equivalent quantity of potassic formate, by which the acid is converted into the aldehyde,

$$\underset{\text{Potassic salt.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\ COKo\end{array}\right.} + \underset{\text{Potassic formate.}}{\left\{\begin{array}{l}H\\ COKo\end{array}\right.} = \underset{\text{Aldehyde.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\ COH\end{array}\right.} + \underset{\text{Potassic carbonate.}}{COKo_2},$$

and subsequent treatment of the aldehyde by nascent hydrogen,

$$\underset{\text{Aldehyde.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\ COH\end{array}\right.} + H_2 = \underset{\text{Normal alcohol.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\ CH_2Ho\end{array}\right.}.$$

3. By the action of sodium amalgam upon a mixture of the acid and chloracid:—

$$3\underset{\text{Acid.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\ COHo\end{array}\right.} + \underset{\text{Chloracid.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\ COCl\end{array}\right.} + 2Na_2 = 3\underset{\text{Sodic salt.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\ CONao\end{array}\right.}$$

$$+ \underset{\text{Alcohol.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\ CH_2Ho\end{array}\right.} + NaCl.$$

The anhydride of the acid is also formed and converted, by the nascent hydrogen evolved by the action of the sodium upon the acid, into alcohol.

Relations of the Normal Fatty Acids to each other. Ascent of the Series.

If the hydrogen constituting the positive part of formic acid were substituted successively by methyl, ethyl, &c., the whole series of normal fatty acids would be obtained :—

Formic acid .... $\left\{\begin{array}{l}H\\COHo\end{array}\right.$.

Acetic acid ...... $\left\{\begin{array}{l}CH_3\\COHo\end{array}\right.$.

Propionic acid .. $\left\{\begin{array}{l}C_2H_5\\COHo\end{array}\right.$.

Butyric acid .... $\left\{\begin{array}{l}C_3H_7\\COHo\end{array}\right.$.

This substitution has not yet been accomplished; but an analogous series of reactions has been effected indirectly with acetic acid.

By the consecutive action of sodium and ethylic iodide upon ethylic acetate, the ethyl salts of butyric and diethacetic acids are obtained. The explanation of this complicated reaction is as follows :—

1. Sodium and ethylic acetate yield ethylic sodaceto-acetate and sodic ethylate, hydrogen being evolved :—

$$2\left\{\begin{array}{l}CH_3\\COEto\end{array}\right. + Na_2 = \left\{\begin{array}{l}CH_3\\CO\\CHNa\\COEto\end{array}\right. + NaEto + H_2.$$

Ethylic acetate. Ethylic sodaceto-acetate. Sodic ethylate.

2. The sodic ethylate acts upon a fresh quantity of ethylic acetate, yielding anew ethylic sodaceto-acetate, together with alcohol :—

$$2\left\{\begin{array}{l}CH_3\\COEto\end{array}\right. + EtNao = \left\{\begin{array}{l}CH_3\\CO\\CHNa\\COEto\end{array}\right. + 2EtHo.$$

Ethylic acetate. Sodic ethylate. Ethylic sodaceto-acetate. Alcohol.

3. If ethylic iodide be now added to the product of the above reactions, the ethylic sodaceto-acetate is converted into ethylic ethaceto-acetate:—

$$\underset{\substack{\text{Ethylic sodaceto-}\\\text{acetate.}}}{\left\{\begin{array}{l}\mathrm{COMe}\\\mathrm{CHNa}\\\mathrm{COEto}\end{array}\right.} + \underset{\substack{\text{Ethylic}\\\text{iodide.}}}{\mathrm{EtI}} = \underset{\substack{\text{Ethylic ethaceto-}\\\text{acetate.}}}{\left\{\begin{array}{l}\mathrm{COMe}\\\mathrm{CEtH}\\\mathrm{COEto}\end{array}\right.} + \underset{\substack{\text{Sodic}\\\text{iodide.}}}{\mathrm{NaI}}.$$

4. The ethylic ethaceto-acetate reacts with sodic ethylate and unaltered acetic ether, yielding ethylic butyrate and sodic acetate:—

$$\underset{\substack{\text{Ethylic ethaceto-}\\\text{acetate.}}}{\left\{\begin{array}{l}\mathrm{COMe}\\\mathrm{CEtH}\\\mathrm{COEto}\end{array}\right.} + \underset{\substack{\text{Sodic}\\\text{ethylate.}}}{\mathrm{EtNao}} + \underset{\substack{\text{Ethylic}\\\text{acetate.}}}{\left\{\begin{array}{l}\mathrm{CH_3}\\\mathrm{COEto}\end{array}\right.} = 2\underset{\substack{\text{Ethylic}\\\text{butyrate.}}}{\left\{\begin{array}{l}\mathrm{CEtH_2}\\\mathrm{COEto}\end{array}\right.}$$

$$+ \underset{\substack{\text{Sodic}\\\text{acetate.}}}{\left\{\begin{array}{l}\mathrm{CH_3}\\\mathrm{CONao}\end{array}\right.}.$$

5. The ethylic butyrate, along with unaltered acetic ether, is acted upon by sodic ethylate, in a reaction corresponding to (2), producing ethylic sodethaceto-acetate:—

$$\underset{\substack{\text{Ethylic}\\\text{butyrate.}}}{\left\{\begin{array}{l}\mathrm{CEtH_2}\\\mathrm{COEto}\end{array}\right.} + \underset{\substack{\text{Ethylic}\\\text{acetate.}}}{\left\{\begin{array}{l}\mathrm{CH_3}\\\mathrm{COEto}\end{array}\right.} + \underset{\substack{\text{Sodic}\\\text{ethylate.}}}{\mathrm{EtNao}} = \underset{\substack{\text{Ethylic}\\\text{sodethaceto-}\\\text{acetate.}}}{\left\{\begin{array}{l}\mathrm{COMe}\\\mathrm{CEtNa}\\\mathrm{COEto}\end{array}\right.} + \underset{\substack{\text{Sodic}\\\text{ethylate.}}}{\mathrm{2EtHo}}.$$

6. The ethylic sodethaceto-acetate and ethylic iodide yield ethylic diethaceto-acetate:—

$$\underset{\substack{\text{Ethylic sodethaceto-}\\\text{acetate.}}}{\left\{\begin{array}{l}\mathrm{COMe}\\\mathrm{CEtNa}\\\mathrm{COEto}\end{array}\right.} + \underset{\substack{\text{Ethylic}\\\text{iodide.}}}{\mathrm{EtI}} = \underset{\substack{\text{Ethylic diethaceto-}\\\text{acetate.}}}{\left\{\begin{array}{l}\mathrm{COMe}\\\mathrm{CEt_2}\\\mathrm{COEto}\end{array}\right.} + \underset{\substack{\text{Sodic}\\\text{iodide.}}}{\mathrm{NaI}}.$$

7. Finally, the ethylic diethaceto-acetate reacts with ethylic acetate and sodic ethylate, the process corresponding to (4),

and forms ethylic diethacetate, ethylic butyrate and sodic acetate.

$$\left\{\begin{matrix}\mathrm{COMe}\\ \mathrm{CEt_2}\\ \mathrm{COEto}\end{matrix}\right. + \left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COEto}\end{matrix}\right. + \mathrm{EtNao} = \left\{\begin{matrix}\mathrm{CEt_2H}\\ \mathrm{COEto}\end{matrix}\right.$$

Ethylic diethaceto-acetate. Ethylic acetate. Sodic ethylate. Ethylic diethacetate.

$$+ \left\{\begin{matrix}\mathrm{CEtH_2}\\ \mathrm{COEto}\end{matrix}\right. + \left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CONao}\end{matrix}\right. .$$

Ethylic butyrate. Sodic acetate.

A method somewhat different from the above, permitting of the separation of the various reactions from each other, and the readier preparation of the ultimate products in a state of purity, consists in starting with ethylic aceto-acetate, $\left\{\begin{matrix}\mathrm{COMe}\\ \mathrm{CH_2}\\ \mathrm{COEto}\end{matrix}\right.$. This compound is obtained from the product of the action of sodium on ethylic acetate, by treating it with acetic acid, by which means hydrogen is substituted for the sodium of the ethylic sodaceto-acetate (see equations 1 and 2). By acting on pure ethylic aceto-acetate with sodium, ethylic sodaceto-acetate, free from the sodic ethylate which is the cause of the various reactions above described, is obtained:—

$$\left\{\begin{matrix}\mathrm{COMe}\\ \mathrm{CH_2}\\ \mathrm{COEto}\end{matrix}\right. + \mathrm{Na} = \left\{\begin{matrix}\mathrm{COMe}\\ \mathrm{CHNa}\\ \mathrm{COEto}\end{matrix}\right. + \mathrm{H}.$$

Ethylic aceto-acetate. Ethylic sodaceto-acetate.

Ethylic iodide is now added, when ethylic ethaceto-acetate is formed by reaction (3). By boiling the latter compound with *concentrated* alcoholic potash, the acetyl group is replaced by hydrogen, whilst potassoxyl takes the place of ethoxyl, a salt of butyric acid being thus formed:—

$$\left\{\begin{matrix}\mathrm{COMe}\\ \mathrm{CEtH}\\ \mathrm{COEto}\end{matrix}\right. + 2\mathrm{KHo} = \left\{\begin{matrix}\mathrm{CEtH_2}\\ \mathrm{COKo}\end{matrix}\right. + \mathrm{COMeKo} + \mathrm{EtHo}.$$

Ethylic ethaceto-acetate. Potassic hydrate. Potassic butyrate. Potassic acetate. Alcohol.

The iodides of other radicals may be substituted for ethylic iodide in the above reaction, by which means higher homologues of butyric acid are obtained. Further, by the action of sodium upon ethylic ethaceto-acetate, ethylic sodethaceto-acetate is formed:—

$$\underset{\text{Ethylic ethaceto-acetate.}}{2\left\{\begin{array}{l}\mathbf{C}\mathrm{OMe}\\ \mathbf{C}\mathrm{EtH}\\ \mathbf{C}\mathrm{OEto}\end{array}\right.} + \mathrm{Na_2} = \underset{\text{Ethylic sodethaceto-acetate.}}{2\left\{\begin{array}{l}\mathbf{C}\mathrm{OMe}\\ \mathbf{C}\mathrm{EtNa}\\ \mathbf{C}\mathrm{OEto}\end{array}\right.} + \mathrm{H_2}.$$

The ethylic sodethaceto-acetate may be subjected to the same series of reactions as the ethylic sodaceto-acetate.

With ethylic iodide it gives ethylic diethaceto-acetate, $\left\{\begin{array}{l}\mathrm{OMe}\\ \mathbf{C}\mathrm{Et_2}\\ \mathbf{C}\mathrm{OEto}\end{array}\right.$, from which, by the action of caustic potash, potassic diethacetate, $\left\{\begin{array}{l}\mathbf{C}\mathrm{Et_2H}\\ \mathbf{C}\mathrm{OKo}\end{array}\right.$, is obtained.

FORMIC ACID.

$$\left\{\begin{array}{l}\mathrm{H}\\ \mathbf{C}\mathrm{OHo}\end{array}\right. \text{ or } \mathbf{C}\mathrm{HOHo}.$$

Molecular weight = 46. *Molecular volume* $\square\!\square$. 1 *litre of formic acid vapour weighs* 23 *criths. Sp. gr. of liquid* 1·223. *Fuses at* 8°·6 C. *Boils at* 99° C.

Occurrence.—If red ants be made to pass over blue litmus-paper and be at the same time irritated, they leave a red streak behind them, produced by the formic acid which they eject. By placing the hand on an ant-hill, a tingling sensation is felt from the same cause, and the hand acquires the powerful and pleasant odour of formic acid.

Formic acid also occurs in the hairs of certain caterpillars and in the sting of nettles.

Formation.—1. Formic acid is produced in a very large number of chemical reactions, as in the oxidation of many organic bodies (such as starch, woody fibre, or tartaric acid) by a mixture of sulphuric acid and manganic oxide, or by potassic hydrate or chromic acid.

2. By the action of potassic hydrate on chloroform, potassic formate is generated :—

$$\underset{\text{Chloroform.}}{\mathbf{C}HCl_3} + \underset{\text{Potassic hydrate.}}{4KHo} = \underset{\text{Potassic formate.}}{\mathbf{C}HOKo} + \underset{\text{Potassic chloride.}}{3KCl} + \underset{\text{Water.}}{2\mathbf{O}H_2}.$$

3. By the oxidation of methylic alcohol :—

$$\underset{\text{Methylic alcohol.}}{\left\{\begin{array}{l}H\\ \mathbf{C}H_2Ho\end{array}\right.} + O_2 = \underset{\text{Formic acid.}}{\left\{\begin{array}{l}H\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

4. By heating equal weights of dry oxalic acid and glycerin together to 75° C., when the oxalic acid splits into formic acid and carbonic anhydride :—

$$\underset{\text{Oxalic acid.}}{\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}OHo\end{array}\right.} = \underset{\text{Formic acid.}}{\left\{\begin{array}{l}H\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Carbonic anhydride.}}{\mathbf{C}O_2}.$$

5. By digesting together at 100°, for forty-eight hours, potassic hydrate and carbonic oxide :—

$$\underset{\text{Potassic hydrate.}}{KHo} + \underset{\text{Carbonic oxide.}}{\mathbf{C}O} = \underset{\text{Potassic formate.}}{\left\{\begin{array}{l}H\\ \mathbf{C}OKo\end{array}\right.}.$$

In like manner, by passing carbonic oxide over soda-lime heated to 200°—250°, sodic formate is formed in large quantity, the porosity of the soda-lime facilitating the absorption of the gas.

6. Formic acid is produced in small quantities by digesting carbon with permanganic acid.

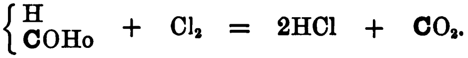
Formic acid from any of these sources is obtained in the concentrated state by decomposing plumbic formate with sulphuretted hydrogen, and afterwards rectifying the acid over plumbic formate :—

$$\underset{\text{Plumbic formate.}}{\begin{array}{l}\mathbf{C}HO\\ \mathbf{C}HO\end{array}Pbo''} + \underset{\text{Sulphuretted hydrogen.}}{\mathbf{S}H_2} = 2\underset{\text{Formic acid.}}{\left\{\begin{array}{l}H\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Plumbic sulphide.}}{\mathbf{Pb}S''}.$$

Character.—When heated with concentrated sulphuric acid, formic acid splits into water and carbonic oxide:—

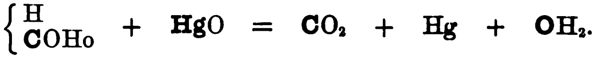
$$\underset{\text{Formic acid.}}{\left\{\begin{matrix}\mathrm{H}\\ \mathrm{COHo}\end{matrix}\right.} = \underset{\text{Carbonic oxide.}}{\mathrm{CO}} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

Chlorine converts formic acid into hydrochloric acid and carbonic anhydride:—



$$\underset{\text{Formic acid.}}{\left\{\begin{matrix}\mathrm{H}\\ \mathrm{COHo}\end{matrix}\right.} + \mathrm{Cl_2} = \underset{\text{Hydrochloric acid.}}{\mathrm{2HCl}} + \underset{\text{Carbonic anhydride.}}{\mathrm{CO_2}}.$$

When heated with excess of mercuric oxide, it is converted into carbonic anhydride and water, the mercury being reduced to the metallic state:—



$$\underset{\text{Formic acid.}}{\left\{\begin{matrix}\mathrm{H}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Mercuric oxide.}}{\mathrm{HgO}} = \underset{\text{Carbonic anhydride.}}{\mathrm{CO_2}} + \mathrm{Hg} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

ACETIC ACID.

$$\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COHo}\end{matrix}\right..$$

Molecular weight = 60. *Molecular volume* $\square\!\square$· 1 *litre of acetic acid vapour weighs* 30 *criths. Sp. gr. of liquid* 1·064. *Fuses at* + 17°. *Boils at* 118°.

Occurrence.—Found in small quantities in the juices of plants and in animal fluids.

Manufacture.—1. By the destructive distillation of wood, a liquid is obtained which contains acetic acid; the acid is purified by being converted first into a calcic, and then into a sodic salt, the latter being afterwards decomposed by sulphuric acid.

2. By the oxidation of ethylic alcohol:—

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_2Ho}\end{matrix}\right.} + \mathrm{O_2} = \underset{\text{Acetic acid.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

Preparation.—Pure acetic acid may be obtained by distilling potassic diacetate:—

$$\underset{\text{Potassic diacetate.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COKo}\end{matrix}\right.,\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COHo}\end{matrix}\right.} = \underset{\text{Potassic acetate.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COKo}\end{matrix}\right.} + \underset{\text{Acetic acid.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COHo}\end{matrix}\right.}\cdot$$

Character.—Chlorine acts on acetic acid in sunlight, producing three chlorinated acids, in which chlorine is substituted for hydrogen:—

$$\underset{\text{Acetic acid.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COHo}\end{matrix}\right.} + \mathrm{Cl_2} = \underset{\text{Monochloracetic acid.}}{\left\{\begin{matrix}\mathrm{CH_2Cl}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}}.$$

$$\underset{\text{Monochloracetic acid.}}{\left\{\begin{matrix}\mathrm{CH_2Cl}\\ \mathrm{COHo}\end{matrix}\right.} + \mathrm{Cl_2} = \underset{\text{Dichloracetic acid.}}{\left\{\begin{matrix}\mathrm{CHCl_2}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}}.$$

$$\underset{\text{Dichloracetic acid.}}{\left\{\begin{matrix}\mathrm{CHCl_2}\\ \mathrm{COHo}\end{matrix}\right.} + \mathrm{Cl_2} = \underset{\text{Trichloracetic acid.}}{\left\{\begin{matrix}\mathrm{CCl_3}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}}.$$

The salts of acetic acid in which the hydrogen of the oxatyl is replaced by monad metals have the general formula

$$\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COMo}\end{matrix}\right.\cdot$$

The acetates of the dyad metals have the constitution represented by the following general formula:—

$$\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CO\text{-}O}\\ \mathrm{CO\text{-}O}\\ \mathrm{CH_3}\end{matrix}\right.\!\!\mathrm{M''} \text{ or } \left\{\begin{matrix}\mathrm{CMeO}\\ \mathrm{Mo''}\\ \mathrm{CMeO}\end{matrix}\right. \text{ or } \begin{matrix}\mathrm{CMeO\text{-}O}\\ \mathrm{CMeO\text{-}O}\end{matrix}\mathrm{M''}.$$

By the action of phosphorous chloride, acetic acid yields acetylic chloride:—

$$3\underset{\text{Acetic acid.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Phosphorous chloride.}}{PCl_3} = 3\underset{\text{Acetylic chloride.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OCl\end{matrix}\right.} + \underset{\text{Phosphorous acid.}}{POHHo_2}.$$

PROPIONIC ACID, *Methacetic Acid.*

$$\left\{\begin{matrix}\mathbf{C}MeH_2\\ \mathbf{C}OHo\end{matrix}\right..$$

Molecular weight = 74. *Molecular volume* $\square\square$. 1 *litre of propionic acid vapour weighs* 37 *criths. Boils at* 141°.

Preparation.—1. By the oxidation of metacetone—a liquid obtained by the distillation of a mixture of sugar and lime.

2. By the action of concentrated solution of potassic hydrate on sugar.

3. By the fermentation of glycerin, and also of sugar, by means of putrid cheese in the presence of calcic carbonate.

4. By the action of potassic hydrate or hydrochloric acid on abnormal ethylic cyanide (see p. 145).

5. By the action of carbonic anhydride on sodic ethide (see p. 146).

6. In very small quantity by the action of carbonic oxide upon sodic ethylate :—

$$\mathbf{C}MeH_2Nao + \mathbf{C}O = \left\{\begin{matrix}\mathbf{C}MeH_2\\ \mathbf{C}ONao\end{matrix}\right..$$

7. By the action of hydriodic acid on lactic acid :—

$$\underset{\text{Lactic acid.}}{\left\{\begin{matrix}\mathbf{C}MeHHo\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Hydriodic acid.}}{2HI} = \underset{\text{Propionic acid.}}{\left\{\begin{matrix}\mathbf{C}MeH_2\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2} + I_2.$$

BUTYRIC ACID, *Ethacetic Acid.*

$$\left\{\begin{matrix}\mathbf{C}EtH_2\\ \mathbf{C}OHo\end{matrix}\right..$$

Molecular weight = 88. *Molecular volume* $\square\square$. 1 *litre of butyric acid vapour weighs* 44 *criths. Sp. gr. of liquid* 0·958. *Fuses at* 0°. *Boils at* 163°.

Occurrence.—In butter, juice of flesh, perspiration, and many animal secretions.

Preparation.—1. By the fermentation of sugar with putrid cheese.

2. By the action of sodium and ethylic iodide on acetic ether (for reaction, see p. 149).

VALERIC ACID, *Valerianic Acid.*

$$\left\{\begin{matrix}\mathrm{CPrH_2}\\ \mathrm{COHo}\end{matrix}\right. .$$

Molecular weight = 102. *Molecular volume* ☐☐. 1 *litre of valeric acid vapour weighs* 51 *criths. Sp. gr. of liquid* 0·9577. *Boils at* 184—185°.

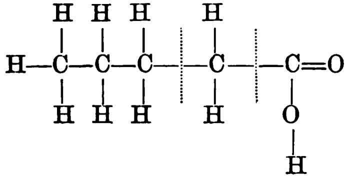
Occurrence.—In many plants, as in the roots of valerian and angelica.

Preparation.—By the oxidation of amylic alcohol with a mixture of sulphuric acid and dipotassic dichromate:—

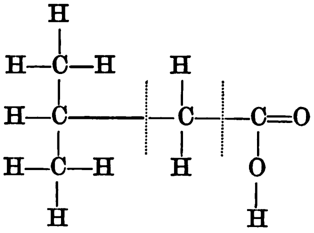
$$\underset{\text{Amylic alcohol.}}{\left\{\begin{matrix}\mathrm{C(C_3H_7)H_2}\\ \mathrm{CH_2Ho}\end{matrix}\right.} + \mathrm{O_2} = \underset{\text{Valeric acid.}}{\left\{\begin{matrix}\mathrm{C(C_3H_7)H_2}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

Isomeric forms.—There are four possible isomers of valeric acid, all of which are known:—

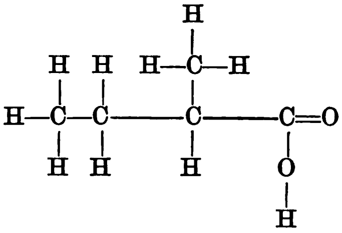
Normal valeric acid or propacetic acid.... $\left\{\begin{matrix}\mathrm{CPrH_2}\\ \mathrm{COHo}\end{matrix}\right.$ or $\left\{\begin{matrix}\mathrm{CH_2(CH_2[CH_2(CH_3)])}\\ \mathrm{COHo}\end{matrix}\right.$.



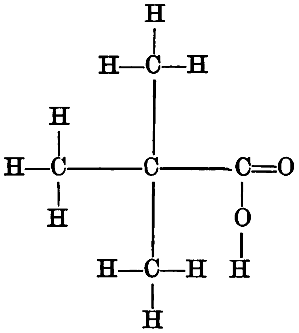
Isopropacetic acid .. $\left\{\begin{matrix}\mathrm{CPr\beta H_2}\\ \mathrm{COHo}\end{matrix}\right.$ or $\left\{\begin{matrix}\mathrm{CH_2[CH(CH_3)_2]}.\\ \mathrm{COHo.}\end{matrix}\right.$



Methethacetic acid.. $\left\{\begin{array}{l}CEtMeH\\COHo\end{array}\right.$ or $\left\{\begin{array}{l}CH(CH_3)[CH_2(CH_3)]\\COHo\end{array}\right.$



Trimethacetic acid .. $\left\{\begin{array}{l}CMe_3\\COHo\end{array}\right.$ or $\left\{\begin{array}{l}C(CH_3)_3\\COHo\end{array}\right.$.



B. *SECONDARY FATTY ACIDS.*

General formula.. $\left\{\begin{array}{l}C(C_nH_{2n+1})_2H\\COHo\end{array}\right.$.

Formation.—1. As ethyl salts by the consecutive substitution of two radicals of the C_nH_{2n+1} series in acetic ether (see p. 149).

2. By the action of a boiling solution of caustic potash upon the nitriles or abnormal cyanides of the secondary radicals.

DIMETHACETIC ACID, *or Isobutyric Acid.*

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{Me_2H}\\ \mathbf{C}\mathbf{O}\mathrm{Ho}\end{array}\right. .$$

Molecular weight = 88. *Molecular volume* ◻◻. 1 *litre of dimethacetic acid vapour weighs* 44 *criths. Boils at* 152°. *Isomeric with butyric or ethacetic acid.*

Preparation.—1. By the series of reactions described on p. 149, substituting methylic iodide for ethylic iodide.

2. By boiling dimethaceto-nitrile with solution of caustic potash:—

$$\underset{\text{Dimethaceto-nitrile.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{Me_2H}\\ \mathbf{C}\mathrm{N'''}\end{array}\right.} + \mathrm{KHo} + \mathbf{O}\mathrm{H_2} = \underset{\text{Potassic dimethacetate.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{Me_2H}\\ \mathbf{C}\mathbf{O}\mathrm{Ko}\end{array}\right.} + \underset{\text{Ammonia.}}{\mathbf{N}\mathrm{H_3}}.$$

Reaction.—By a hot solution of chromic acid dimethacetic acid is decomposed into carbonic anhydride and acetic acid:—

$$\underset{\text{Dimethacetic acid.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{Me_2H}\\ \mathbf{C}\mathbf{O}\mathrm{Ho}\end{array}\right.} + 3\mathrm{O_2} = 2\mathbf{C}\mathrm{O_2} + 2\mathbf{O}\mathrm{H_2} + \underset{\text{Acetic acid.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathbf{O}\mathrm{Ho}\end{array}\right.}.$$

Acetone is sometimes formed as an intermediate product.

Diethacetic acid, $\left\{\begin{array}{l}\mathbf{C}\mathrm{Et_2H}\\ \mathbf{C}\mathbf{O}\mathrm{Ho}\end{array}\right.$, isomeric with caproic acid, and *diamylacetic acid*, $\left\{\begin{array}{l}\mathbf{C}\mathrm{Ay_2H}\\ \mathbf{C}\mathbf{O}\mathrm{HO}\end{array}\right.$, isomeric with lauric acid, have been prepared by the substitution of ethylic and amylic iodides in the above reaction.

C. *TERTIARY FATTY ACIDS.*

General formula.. $\left\{\begin{matrix} C(C_nH_{2n+1})_3. \\ COHo \end{matrix}\right.$

Only one acid belonging to this division is known.

TRIMETHACETIC ACID.

$$\left\{\begin{matrix} CMe_3 \\ COHo \end{matrix}\right. \cdot$$

Molecular weight = 102. *Molecular volume* □□· 1 *litre of trimethacetic acid vapour weighs* 51 *criths. Isomeric with valeric acid. Fuses at* 35°·5. *Boils at* 163°·8.

For the graphic formula of trimethacetic acid see p. 158.

Preparation.—By boiling tertiary butylic abnormal cyanide with alcoholic potash :—

$$\underset{\substack{\text{Tertiary}\\ \text{valero-}\\ \text{nitrile.}}}{\left\{\begin{matrix} CMe_3 \\ CN''' \end{matrix}\right.} + \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{KHo} + \underset{\text{Water.}}{OH_2} = \underset{\substack{\text{Potassic}\\ \text{trimethacetate.}}}{\left\{\begin{matrix} CMe_3 \\ COKo \end{matrix}\right.} + \underset{\text{Ammonia.}}{NH_3}.$$

CHAPTER XVII.

THE ACIDS.

2. *ACRYLIC OR OLEIC SERIES OF ACIDS.*

General formula of normal and secondary acids .... $\left\{\begin{matrix} C(C_nH_{2n})''(C_mH_{2m+1}) \\ COHo \end{matrix}\right. \cdot$

This series is divided into normal, secondary, and olefine acids. In the normal acids $m = 0$; in the secondary it must be a positive integer.

Most of the normal acids exist as ethereal salts of glycerin in natural fats and oils.

The following is a list of the acrylic series of acids:—

A. *NORMAL ACIDS.*

Acrylic acid	$\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{COHo}\end{array}\right.$	or	$\left\{\begin{array}{l}\mathrm{C(CH_2)''H}\\ \mathrm{COHo}\end{array}\right.$.
Crotonic acid	$\left\{\begin{array}{l}\mathrm{CEt''H}\\ \mathrm{COHo}\end{array}\right.$	or	$\left\{\begin{array}{l}\mathrm{C(CMeH)''H}\\ \mathrm{COHo}\end{array}\right.$.
Angelic acid	$\left\{\begin{array}{l}\mathrm{CPr''H}\\ \mathrm{COHo}\end{array}\right.$	or	$\left\{\begin{array}{l}\mathrm{C(C_3H_6)''H}\\ \mathrm{COHo}\end{array}\right.$.
Pyroterebic acid Hydrosorbic acid	$\left\{\begin{array}{l}\mathrm{CBu''H}\\ \mathrm{COHo}\end{array}\right.$	or	$\left\{\begin{array}{l}\mathrm{C(C_4H_8)''H}\\ \mathrm{COHo}\end{array}\right.$.
Damaluric acid			$C_7H_{12}O_2$.
Damolic acid			$C_{13}H_{24}O_2$.
Moringic acid Cimicic acid			$C_{15}H_{28}O_2$.
Physetoleic acid Hypogæic acid Gaïdic acid			$C_{16}H_{30}O_2$.
Oleic acid			$\left\{\begin{array}{l}\mathrm{C(C_{16}H_{32})''H}\\ \mathrm{COHo}\end{array}\right.$.
Elaïdic acid			$C_{18}H_{34}O_2$.
Doeglic acid			$C_{19}H_{36}O_2$.
Brassic acid. (*Erucic acid*)			$C_{22}H_{42}O_2$.

B. *SECONDARY ACIDS.*

Methacrylic acid	$\left\{\begin{array}{l}\mathrm{CMe''Me}\\ \mathrm{COHo}\end{array}\right.$	or	$\left\{\begin{array}{l}\mathrm{C(CH_2)''(CH_3)}\\ \mathrm{COHo}\end{array}\right.$.
Methylcrotonic acid	$\left\{\begin{array}{l}\mathrm{CEt''Me}\\ \mathrm{COHo}\end{array}\right.$	or	$\left\{\begin{array}{l}\mathrm{C(C_2H_4)''(CH_3)}\\ \mathrm{COHo}\end{array}\right.$.
Ethylcrotonic acid	$\left\{\begin{array}{l}\mathrm{CEt''Et}\\ \mathrm{COHo}\end{array}\right.$	or	$\left\{\begin{array}{l}\mathrm{C(C_2H_4)''(C_2H_5)}\\ \mathrm{COHo}\end{array}\right.$.

C. *OLEFINE ACIDS.*

β-Crotonic acid	$\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.$	or	$\left\{\begin{array}{l}\mathrm{C(CH_2)''H}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.$.

Formation of Normal Acids.—1. By the oxidation of the alcohols of the allyl or $C_nH_{2n-1}Ho$ series:—

$$\underset{\text{Alcohol.}}{\left\{\begin{matrix}\mathbf{C}(C_nH_{2n})''H\\ \mathbf{C}H_2Ho\end{matrix}\right.} + O_2 = \underset{\text{Acid.}}{\left\{\begin{matrix}\mathbf{C}(C_nH_{2n})''H\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

2. By the oxidation of the aldehydes of the acrolein or $\left\{\begin{matrix}\mathbf{C}(C_nH_{2n})''H\\ \mathbf{C}OH\end{matrix}\right.$ series:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{matrix}\mathbf{C}(C_nH_{2n})''H\\ \mathbf{C}OH\end{matrix}\right.} + O = \underset{\text{Acid.}}{\left\{\begin{matrix}\mathbf{C}(C_nH_{2n})''H\\ \mathbf{C}OHo\end{matrix}\right.}.$$

Formation of Secondary Acids.—By the action of phosphorous chloride, phosphoric chloride, phosphoric oxytrichloride or phosphoric anhydride upon the ethereal salts of secondary acids of the lactic series, the elements of water are removed and the ethereal salts of the acrylic secondary divisions of acid produced:—

$$\underset{\substack{\text{Ethereal salt of}\\ \text{the lactic series.}}}{3\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})_2Ho\\ \mathbf{C}OEto\end{matrix}\right.} + \underset{\substack{\text{Phosphorous}\\ \text{chloride.}}}{\mathbf{P}Cl_3} = \underset{\substack{\text{Ethereal salt of}\\ \text{the acrylic series.}}}{3\left\{\begin{matrix}\mathbf{C}(C_nH_{2n})''(C_nH_{2n+1})\\ \mathbf{C}OEto\end{matrix}\right.}$$

$$+ \underset{\substack{\text{Phosphorous}\\ \text{acid.}}}{\mathbf{P}OHHo_2} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{3HCl}.$$

Relations of the Acrylic to the Acetic Series of Acids.

The normal and secondary acids of the acrylic series, when treated with fused potassic hydrate, yield the potassic salts of two normal acids of the acetic series:—

$$\underset{\text{Acid of the acrylic series.}}{\left\{\begin{matrix}\mathbf{C}(C_nH_{2n})''(C_mH_{2m+1})\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{2KHo} = \underset{\substack{\text{Potassic salt of acid}\\ \text{of the acetic series.}}}{\left\{\begin{matrix}\mathbf{C}(C_mH_{2m+1})H_2\\ \mathbf{C}OKo\end{matrix}\right.}$$

$$+ \underset{\substack{\text{Potassic salt of acid}\\ \text{of the acetic series.}}}{\left\{\begin{matrix}\mathbf{C}(C_{n-2}H_{2n-3})H_2\\ \mathbf{C}OKo\end{matrix}\right.} + H_2.$$

All the members of the acrylic series found in nature give acetic acid as one of the acids produced in this reaction. From this and other considerations, it is believed that their positive radicals all contain one atom of hydrogen and a dyad radical. They are normal acids; and by the action of fused potassic hydrate the dyad radical becomes substituted by two atoms of hydrogen. Thus:—

$$\begin{array}{cccccccc} \left\{\begin{matrix}\mathbf{C}\mathrm{Me''H}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. & + & \mathrm{2KHo} & = & \left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. & + & \left\{\begin{matrix}\mathrm{H}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. & + \mathrm{H_2}. \\ \text{Acrylic acid.} & & \text{Potassic hydrate.} & & \text{Potassic acetate.} & & \text{Potassic formate.} & \end{array}$$

$$\begin{array}{cccccccc} \left\{\begin{matrix}\mathbf{C}\mathrm{(CMeH)''H}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. & + & \mathrm{2KHo} & = & \left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. & + & \left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. & + \mathrm{H_2}. \\ \text{Crotonic acid.} & & \text{Potassic hydrate.} & & \text{Potassic acetate.} & & \text{Potassic acetate.} & \end{array}$$

$$\begin{array}{cccccccc} \left\{\begin{matrix}\mathbf{C}\mathrm{Pr''H}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. & + & \mathrm{2KHo} & = & \left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. & + & \left\{\begin{matrix}\mathbf{C}\mathrm{MeH_2}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. & + \mathrm{H_2}. \\ \text{Angelic acid.} & & \text{Potassic hydrate.} & & \text{Potassic acetate.} & & \text{Potassic propionate.} & \end{array}$$

Some of the secondary acids also give acetic acid when treated with fused potassic hydrate; but this can only happen when the dyad radical contains two atoms of carbon, thus:—

$$\begin{array}{cccccccc} \left\{\begin{matrix}\mathbf{C}\mathrm{Me''Me}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. & + & \mathrm{2KHo} & = & \left\{\begin{matrix}\mathbf{C}\mathrm{MeH_2}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. & + & \left\{\begin{matrix}\mathrm{H}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. & + \mathrm{H_2}. \\ \text{Methacrylic acid.} & & \text{Potassic hydrate.} & & \text{Potassic propionate.} & & \text{Potassic formate.} & \end{array}$$

$$\begin{array}{cccccccc} \left\{\begin{matrix}\mathbf{C}\mathrm{(CMeH)''Me}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. & + & \mathrm{2KHo} & = & \left\{\begin{matrix}\mathbf{C}\mathrm{MeH_2}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. & + & \left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. & + \mathrm{H_2}. \\ \text{Methylcrotonic acid.} & & \text{Potassic hydrate.} & & \text{Potassic propionate.} & & \text{Potassic acetate.} & \end{array}$$

$$\begin{array}{cccccccc} \left\{\begin{matrix}\mathbf{C}\mathrm{(CMeH)''Et}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. & + & \mathrm{2KHo} & = & \left\{\begin{matrix}\mathbf{C}\mathrm{EtH_2}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. & + & \left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. & + \mathrm{H_2}. \\ \text{Ethylcrotonic acid.} & & \text{Potassic hydrate.} & & \text{Potassic butyrate.} & & \text{Potassic acetate.} & \end{array}$$

ACRYLIC ACID.

$$\left\{\begin{matrix}\mathbf{C}\mathrm{Me''H}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. .$$

Molecular weight = 72. *Fuses at* 7°. *Boils at* 139—140.°

Preparation.—By the oxidation of acrolein with argentic oxide:—

$$\underset{\text{Acrolein.}}{\left\{\begin{matrix}\mathrm{CMe''H}\\ \mathrm{COH}\end{matrix}\right.} + \underset{\text{Argentic oxide.}}{\mathrm{OAg_2}} = \underset{\text{Acrylic acid.}}{\left\{\begin{matrix}\mathrm{CMe''H}\\ \mathrm{COHo}\end{matrix}\right.} + \mathrm{Ag_2}.$$

Reactions.—1. Acrylic acid, under the influence of nascent hydrogen, is converted very slowly into propionic acid:—

$$\underset{\text{Acrylic acid.}}{\left\{\begin{matrix}\mathrm{CMe''H}\\ \mathrm{COHo}\end{matrix}\right.} + \mathrm{H_2} = \underset{\text{Propionic acid.}}{\left\{\begin{matrix}\mathrm{CMeH_2}\\ \mathrm{COHo}\end{matrix}\right.}.$$

2. Acrylic acid also combines directly with bromine, producing dibromopropionic acid.

3. It also combines directly with hydrochloric, hydrobromic, and hydriodic acid, yielding β-chlor-, β-brom-, and β-iodopropionic acid.

OLEIC ACID.

$$\left\{\begin{matrix}\mathrm{C(C_{16}H_{32})''H}\\ \mathrm{COHo}\end{matrix}\right..$$

Preparation.—Obtained in the purification of stearic acid.

Reaction.—Heated with potassic hydrate, it gives potassic acetate and palmitate:—

$$\underset{\text{Oleic acid.}}{\left\{\begin{matrix}\mathrm{C(C_{16}H_{32})''H}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{\mathrm{2KHo}} = \underset{\text{Potassic acetate.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COKo}\end{matrix}\right.} + \underset{\text{Potassic palmitate.}}{\left\{\begin{matrix}\mathrm{C(C_{14}H_{29})H_2}\\ \mathrm{COKo}\end{matrix}\right.} + \mathrm{H_2}.$$

CHAPTER XVIII.

THE ACIDS.

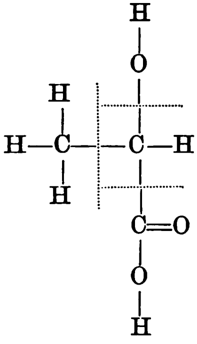
3. *LACTIC SERIES OF ACIDS.*

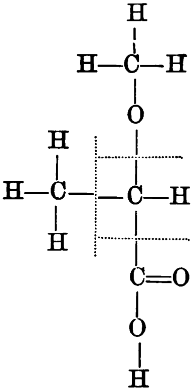
General formula of normal and secondary acids:—

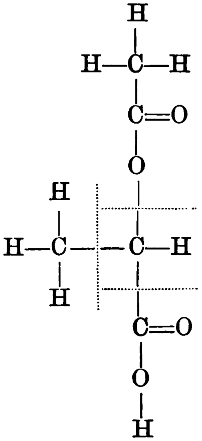
$$\left\{\begin{matrix}\mathrm{C(C_{\mathit{n}}H_{2\mathit{n}+1})(C_{\mathit{m}}H_{2\mathit{m}+1})Ho}\\ \mathrm{COHo}\end{matrix}\right..$$

In the normal acids *m* in this formula $= 0$; but in the secondary acids it must be a positive integer.

The members of the lactic series may be defined as acids containing one semimolecule of oxatyl, the fourth bond of the carbon of which is united with the carbon of a positive group containing one semimolecule of hydroxyl, or of the peroxide of a monad organic radical either positive or negative. The following examples will serve to illustrate this definition:—


Lactic acid.


Methyl-lactic acid.


Aceto-lactic acid.

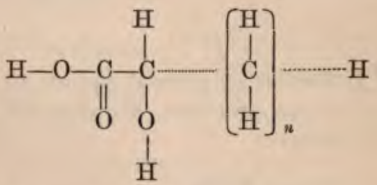
The acids of this series at present known, or which could be obtained by obvious processes, are classified into the following eight divisions:—

1. Normal Acids.
2. Etheric Normal Acids.
3. Secondary Acids.
4. Etheric Secondary Acids.
5. Normal Olefine Acids.
6. Etheric Normal Olefine Acids.
7. Secondary Olefine Acids.
8. Etheric Secondary Olefine Acids.

1st. *Normal Acids.*—A normal acid of the lactic series may be defined as one in which an atom of carbon is united with oxatyl, hydroxyl, and at least one atom of hydrogen. The general formula of these acids is therefore

$$\left\{\begin{matrix}\mathbf{C}\overset{+}{R}HHo \\ \mathbf{C}OHo\end{matrix}\right. .$$

In this formula $\overset{+}{R}$ may be either hydrogen or any monad positive organic radical. The number of acids possessing the same atomic weight, and belonging to this division, is determined by the number of isomeric modifications of which the positive organic radical is susceptible. Thus, in the acids containing two, three, or four atoms of carbon, there can be only one of each belonging to this division, because these acids cannot contain a positive organic radical higher in the series than ethyl, and this radical is not susceptible of isomeric modification; but a normal acid containing propyl can have one isomer in this division, the two acids containing respectively propyl ($\mathbf{C}EtH_2$) and isopropyl ($\mathbf{C}Me_2H$). For acids of this division containing normal positive organic radicals only, the following general graphic formula may be given:—



In the case of glycollic acid $n = 0$.

The following are the acids at present known belonging to this division:—

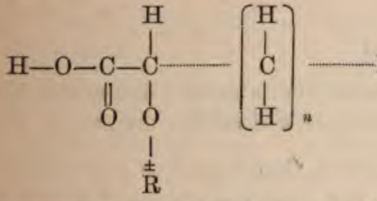
Glycollic acid..........	$\left\{\begin{matrix}\mathbf{C}H_2Ho \\ \mathbf{C}OHo\end{matrix}\right. .$
Lactic acid............	$\left\{\begin{matrix}\mathbf{C}MeHHo \\ \mathbf{C}OHo\end{matrix}\right. .$

α-Oxybutyric acid...... $\left\{\begin{array}{l}\mathbf{CEtHHo}\\ \mathbf{COHo}\end{array}\right.$.

Isovalerolactic acid .... $\left\{\begin{array}{l}\mathbf{C\beta PrHHo}\\ \mathbf{COHo}\end{array}\right.$.

*Leucic acid .... $\left\{\begin{array}{l}\mathbf{CBuHHo}\\ \mathbf{COHo}\end{array}\right.$.

2nd. *Etheric Normal Acids.*—An etheric normal acid of the lactic series is constituted like a normal acid, but contains a monad organic radical, positive or negative, in the place of the hydrogen of the *non-oxatylic* hydroxyl. The following is therefore the general formula of these acids: in the graphic formula n, as before, may = 0.



or $\left\{\begin{array}{l}\mathbf{C\overset{+}{R}H\overset{\pm}{R}o}\\ \mathbf{COHo}\end{array}\right.$.

The number of possible isomers belonging to this division is very great; for, in addition to those of which the normal acids containing $\overset{+}{\mathrm{R}}$ of the same value are susceptible, a host of others must result from the complementary variation of $\overset{+}{\mathrm{R}}$ and $\overset{\pm}{\mathrm{R}}$. The lowest member of the division, methylglycollic acid (isomeric with lactic acid), is the only one incapable of isomeric modification.

The following examples will serve to illustrate the constitution of the acids belonging to this division:—

Methylglycollic acid...... $\left\{\begin{array}{l}\mathbf{CH_2Meo}\\ \mathbf{COHo}\end{array}\right.$.

Ethyl-lactic acid .... $\left\{\begin{array}{l}\mathbf{CMeHEto}\\ \mathbf{COHo}\end{array}\right.$.

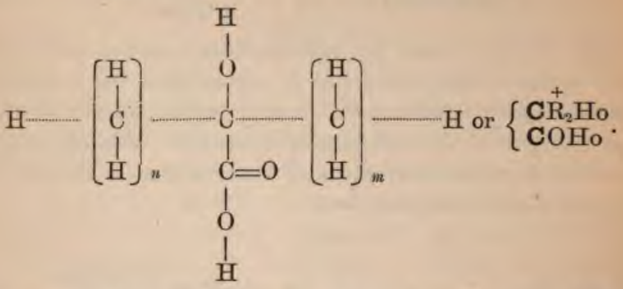
Aceto-lactic acid .... $\left\{\begin{array}{l}\mathbf{CMeHAco}\dagger\\ \mathbf{COHo}\end{array}\right.$.

---

* Or perhaps $\left\{\begin{array}{l}\mathbf{C\beta BuHHo}\\ \mathbf{COHo}\end{array}\right.$.

† Aco = peroxide of acetyl, $C_2H_3O_2$.

3rd. *Secondary Acids.*—A secondary acid of the lactic series is one in which an atom of carbon is united with oxatyl, hydroxyl, and *two semimolecules* of a monad positive organic radical. The general formula of these acids is:—



$$\mathrm{H}\cdots\left[\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right]_n\cdots\begin{array}{c}\mathrm{H}\\|\\\mathrm{O}\\|\\\mathrm{C}\\|\\\mathrm{C{=}O}\\|\\\mathrm{O}\\|\\\mathrm{H}\end{array}\cdots\left[\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right]_m\cdots\mathrm{H}\text{ or }\left\{\begin{array}{l}\mathrm{C\overset{+}{R}_2Ho}\\\mathrm{COHo}\end{array}\right..$$

In the graphic expression, the values of n and m may differ; but both are positive integers, and neither may $= 0$. In the symbolic formula $\overset{+}{\mathrm{R}}$ must be a monad positive organic radical. The following example will serve to illustrate their constitution:—

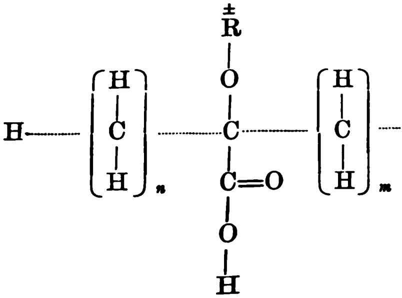
Dimethoxalic acid........ $\left\{\begin{array}{l}\mathrm{CMe_2Ho}\\\mathrm{COHo}\end{array}\right..$

Ethomethoxalic acid...... $\left\{\begin{array}{l}\mathrm{CEtMeHo}\\\mathrm{COHo}\end{array}\right..$

Diethoxalic acid .... $\left\{\begin{array}{l}\mathrm{CEt_2Ho}\\\mathrm{COHo}\end{array}\right..$

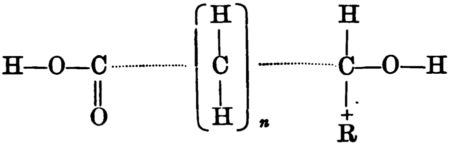
The number of acids possessing the same atomic weight, and belonging to this division, is determined, first, by the complementary variation of the two positive radicals, and, secondly, by the number of possible isomers of these radicals. The lowest two terms of the series are alone incapable of isomeric modification by either of the causes mentioned.

4th. *Etheric Secondary Acids.*—These acids stand in the same relation to the secondary as the etheric normal to the normal acids; they consequently contain a monad organic radical in the place of the hydrogen of the non-oxatylic hydroxyl. The following is therefore the general formula of these acids:—



$$\mathrm{H}-\left[\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right]_n\cdots\cdots\begin{array}{c}\overset{\pm}{\mathrm{R}}\\|\\\mathrm{O}\\|\\\mathrm{C}\\|\\\mathrm{C}{=}\mathrm{O}\\|\\\mathrm{O}\\|\\\mathrm{H}\end{array}-\left[\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right]_m\cdots\cdots\mathrm{H}\quad\text{or}\quad\left\{\begin{array}{l}\mathrm{C\overset{+}{R}_2\overset{\pm}{R}o}\\\mathrm{COHo}\end{array}\right..$$

5th. *Normal Olefine Acids.*—A normal olefine acid belonging to the lactic series is one in which the atom of carbon united with oxatyl is *not* combined with hydroxyl, and in which the atom of carbon united with hydroxyl is combined with not less than one atom of hydrogen. The following are the general graphic and symbolic formulæ of the acids belonging to this division:—



$$\mathrm{H{-}O{-}}\begin{array}{c}\mathrm{C}\\\|\\\mathrm{O}\end{array}\cdots\cdots\left[\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right]_n\cdots\cdots\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\overset{+}{\mathrm{R}}\end{array}\mathrm{{-}O{-}H}\quad\text{or}\quad\left\{\begin{array}{l}\mathrm{C\overset{+}{R}HHo}\\(\mathrm{CH_2})_n\\\mathrm{COHo}\end{array}\right..$$

In both these formulæ n must be a positive integer and cannot $= 0$, but $\overset{+}{\mathrm{R}}$ may be either hydrogen or a monad positive organic radical. The olefines of these acids may belong either to the ethylene or ethylidene series.

The following are the only acids at present known belonging to this division:—

Hydracrylic acid .... $\left\{\begin{array}{l}\mathrm{CH_2Ho}\\\mathrm{CH_2}\\\mathrm{COHo}\end{array}\right..$

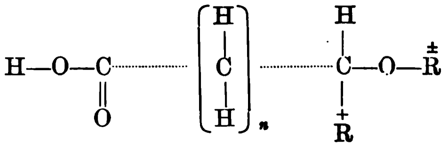
β-Oxybutyric acid .... $\left\{\begin{array}{l}\mathrm{CMeHHo}\\\mathrm{CH_2}\\\mathrm{COHo}\end{array}\right..$

γ-Oxybutyric acid.......... $\left\{\begin{array}{l} CH_2Ho \\ CH_2 \\ CH_2 \\ COHo \end{array}\right.$

α-Methyl-β-oxybutyric acid.. $\left\{\begin{array}{l} CMeHHo \\ CMeH \\ COHo \end{array}\right.$

The number of isomers in this division will obviously depend, first, upon the complementary variations of $\overset{+}{R}$ and $(CH_2)_n$; secondly, upon the isomeric modifications of which $\overset{+}{R}$ is susceptible; and thirdly, upon the isomeric modifications of $(CH_2)_n$.

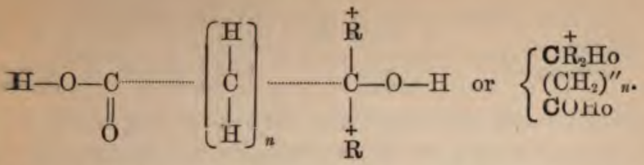
6th. *Etheric Normal Olefine Acids.*—These acids only differ from the normal olefine acids in having the hydrogen of the non-oxatylic hydroxyl replaced by an organic monad radical, positive or negative; their general formula is therefore:—



$$H—O—\underset{\underset{O}{\|}}{C}\cdots\cdots\left[\begin{array}{c}H\\ |\\ C\\ |\\ H\end{array}\right]_n\cdots\cdots\overset{\overset{H}{|}}{\underset{\underset{\overset{+}{R}}{|}}{C}}—O—\overset{\pm}{R} \quad \text{or} \quad \left\{\begin{array}{l} C\overset{+}{R}H\overset{\pm}{R}o \\ (CH_2)''_n \\ COHo \end{array}\right.$$

As in the fifth division, *n* must be a positive integer and cannot = 0, whilst $\overset{+}{R}$ may be either hydrogen or a monad positive organic radical; but $\overset{\pm}{R}$ must be a monad organic radical, either positive or negative.

7th. *Secondary Olefine Acids.*—A secondary olefine acid of this series is one in which the atom of carbon united with oxatyl is *not* combined with hydroxyl, and in which the atom of carbon united with hydroxyl is also combined with two monad positive organic radicals, as shown in the following formulæ:—



$$H-O-\underset{\underset{O}{\|}}{C}\cdots\cdots\left[\begin{array}{c}H\\|\\C\\|\\H\end{array}\right]_n\cdots\cdots\overset{\overset{+}{R}}{\underset{\underset{+}{R}}{\overset{|}{\underset{|}{C}}}}-O-H \quad \text{or} \quad \left\{\begin{array}{l}C\overset{+}{R}_2Ho\\(CH_2)''_n.\\COHo\end{array}\right.$$

In both of these formulæ n must be a positive integer and cannot $= 0$, and $\overset{+}{R}$ must be a monad positive radical.

8th. *Etheric Secondary Olefine Acids.*—These acids are related to the secondary olefine acids in the same way as the sixth division to the fifth. No member of the eighth division has yet been formed.

Formation of the Normal Acids.—1. By the oxidation of the glycols, or dihydric alcohols:—

$$\underset{\text{Glycol.}}{\left\{\begin{array}{l}CH_2Ho\\CH_2Ho\end{array}\right.} + O_2 = \underset{\text{Glycollic acid.}}{\left\{\begin{array}{l}CH_2Ho\\COHo\end{array}\right.} + \underset{\text{Water.}}{OH_2}.$$

2. By the oxidation of the $C_nH_{2n+1}Ho$ alcohols:—

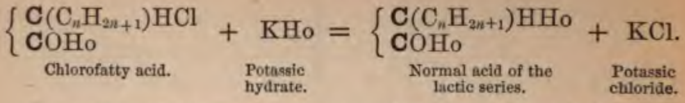
$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{array}{l}CH_3\\CH_2Ho\end{array}\right.} + 3O = \underset{\text{Glycollic acid.}}{\left\{\begin{array}{l}CH_2Ho\\COHo\end{array}\right.} + \underset{\text{Water.}}{OH_2}.$$

3. By the action of aqueous hydrochloric acid upon the cyanhydrates of the aldehydes:—

$$\underset{\text{Ethylidenic cyanhydrate.}}{\left\{\begin{array}{l}CMeHHo\\CN\end{array}\right.} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Lactic acid.}}{\left\{\begin{array}{l}CMeHHo\\COHo\end{array}\right.} + \underset{\text{Ammonia.}}{NH_3}.$$

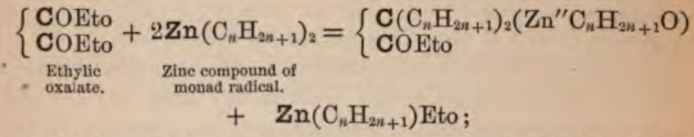
4. From the fatty acids, by converting them first into chloro-substitution acids, and then acting upon these compounds with potassic hydrate:—

$$\underset{\text{Fatty acid.}}{\left\{\begin{array}{l}C(C_nH_{2n+1})H_2\\COHo\end{array}\right.} + Cl_2 = \underset{\text{Chlorofatty acid.}}{\left\{\begin{array}{l}C(C_nH_{2n+1})HCl\\COHo\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{HCl};$$

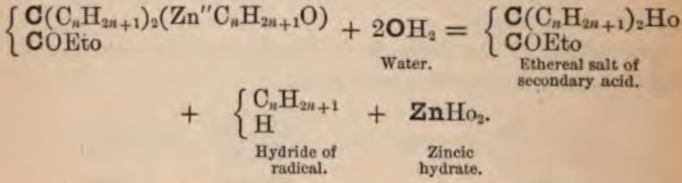


$$\underset{\text{Chlorofatty acid.}}{\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})HCl\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Normal acid of the lactic series.}}{\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})HHo\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Potassic chloride.}}{KCl.}$$

Formation of Secondary Acids.—By the action of the zinc compounds of the monad positive organic radicals upon ethylic oxalate, and the subsequent addition of water:—

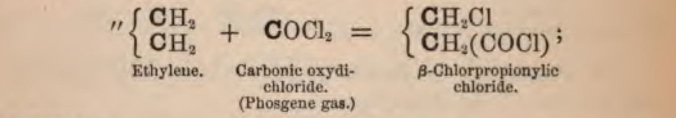


$$\underset{\text{Ethylic oxalate.}}{\left\{\begin{matrix}\mathbf{C}OEto\\ \mathbf{C}OEto\end{matrix}\right.} + \underset{\text{Zinc compound of monad radical.}}{2\mathbf{Zn}(C_nH_{2n+1})_2} = \left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})_2(Zn''C_nH_{2n+1}O)\\ \mathbf{C}OEto\end{matrix}\right.$$
$$+ \quad \mathbf{Zn}(C_nH_{2n+1})Eto;$$

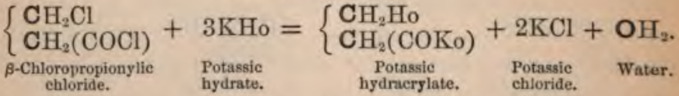


$$\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})_2(Zn''C_nH_{2n+1}O)\\ \mathbf{C}OEto\end{matrix}\right. + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Ethereal salt of secondary acid.}}{\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})_2Ho\\ \mathbf{C}OEto\end{matrix}\right.}$$
$$+ \quad \underset{\text{Hydride of radical.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ H\end{matrix}\right.} + \underset{\text{Zincic hydrate.}}{\mathbf{Zn}Ho_2.}$$

Formation of Olefine Acids.—1. By uniting a dyad positive organic radical with carbonic oxydichloride (*phosgene gas*) under the influence of sunlight, and subsequently acting upon the product with potassic hydrate:—

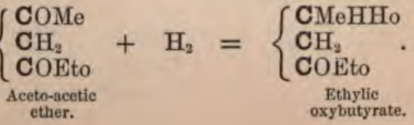


$$\underset{\text{Ethylene.}}{''\left\{\begin{matrix}\mathbf{C}H_2\\ \mathbf{C}H_2\end{matrix}\right.} + \underset{\text{Carbonic oxydichloride. (Phosgene gas.)}}{\mathbf{C}OCl_2} = \underset{\beta\text{-Chlorpropionylic chloride.}}{\left\{\begin{matrix}\mathbf{C}H_2Cl\\ \mathbf{C}H_2(COCl)\end{matrix}\right.};$$



$$\underset{\beta\text{-Chloropropionylic chloride.}}{\left\{\begin{matrix}\mathbf{C}H_2Cl\\ \mathbf{C}H_2(COCl)\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{3KHo} = \underset{\text{Potassic hydracrylate.}}{\left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}H_2(COKo)\end{matrix}\right.} + \underset{\text{Potassic chloride.}}{2KCl} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

2. By the action of nascent hydrogen on compounds of the aceto-acetic ether type. Thus from aceto-acetic ether itself ethylic β-oxybutyrate is obtained:—



$$\underset{\text{Aceto-acetic ether.}}{\left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}H_2\\ \mathbf{C}OEto\end{matrix}\right.} + H_2 = \underset{\text{Ethylic oxybutyrate.}}{\left\{\begin{matrix}\mathbf{C}MeHHo\\ \mathbf{C}H_2\\ \mathbf{C}OEto\end{matrix}\right.}.$$

Relations of the Lactic to the Acetic Series of Acids.

1. The transformation of the acetic or fatty into the normal lactic series of acids has been mentioned above (p. 171).

2. The converse operation is effected with the normal and secondary acids of the lactic series by means of hydriodic acid:—

$$\underset{\text{Acid of lactic series.}}{\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})(C_mH_{2m+1})Ho\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Hydriodic acid.}}{2HI} = \underset{\text{Acid of acetic series.}}{\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})(C_mH_{2m+1})H\\ \mathbf{C}OHo\end{array}\right.}$$

$$+ \underset{\text{Water.}}{\mathbf{O}H_2} + I_2.$$

If m does not $= 0$, the fatty acid will be a secondary one, like the member of the lactic series from which it is derived.

Relations of the Lactic to the Acrylic Series of Acids.

If the ethereal salts of the secondary acids of the lactic series be treated with phosphorus chloride, phosphoric chloride, phosphoric oxychloride, or phosphoric anhydride, the ethereal salts of the secondary acids of the acrylic series are produced:—

$$\underset{\text{Ethereal salt of lactic series.}}{3\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})(C_mH_{2m+1})Ho\\ \mathbf{C}OEto\end{array}\right.} + \underset{\text{Phosphorous chloride.}}{\mathbf{P}Cl_3} = \underset{\text{Ethereal salt of acrylic series.}}{3\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})(C_mH_{2m})''\\ \mathbf{C}OEto\end{array}\right.}$$

$$+ \underset{\text{Phosphorous acid.}}{\mathbf{P}OHHo_2} + \underset{\text{Hydrochloric acid.}}{3HCl.}$$

This reaction has not yet been accomplished with the normal acids of the lactic series.

A secondary lactic acid *minus* $\mathbf{O}H_2$ = an acrylic acid. The reverse of this operation has not been performed.

LACTIC ACID.

$$\left\{\begin{array}{l}\mathbf{C}MeHHo\\ \mathbf{C}OHo\end{array}\right. .$$

Sp. gr. of liquid 1·215.

Occurrence.—In sour milk, *Sauerkraut*, fluids of muscular tissue, gastric juice, saliva of diabetic patients. In the acid liquor of starch-factories, in blood, urine, tears, bile, &c. It is also a general product of putrefactive fermentation. The acid contained in animal fluids is *paralactic acid* (see below).

Preparation.—By fermenting sugar with putrid cheese.

For other processes, see pages 171 and 172.

Its salts have the following general formulæ:—

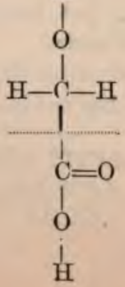
$$\left\{\begin{matrix}\mathbf{C}\mathrm{MeHHo} \\ \mathbf{C}\mathrm{OMo}\end{matrix}\right. . \qquad \begin{matrix}\left\{\begin{matrix}\mathbf{C}\mathrm{MeHHo} \\ \mathbf{C}\mathrm{O\text{-}O}\end{matrix}\right. \\ \left\{\begin{matrix}\mathbf{C}\mathrm{O\text{-}O} \\ \mathbf{C}\mathrm{MeHHo}\end{matrix}\right.\end{matrix}\mathrm{M}'' .$$

Salts of monad metals. Salts of dyad metals.

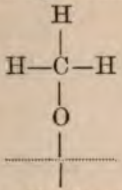
Paralactic acid, the acid contained in the animal juices, differs from ordinary lactic acid in its action on the ray of polarised light, which it causes to rotate to the right, whilst ordinary lactic acid is without action on the polarised ray. Both acids have, however, the same chemical constitution. The difference in their properties is dependent upon what is known as *physical isomerism*, occasioned by the presence of an *asymmetric carbon atom* (see under tartaric acid).

Isomerism in the Lactic Series.

The synthetical study of the acids of this series affords an insight into numerous and interesting cases of isomerism. Commencing with the lowest member of the series, we have for glycollic acid the formula



An inspection of this formula shows that glycollic acid admits of no isomeric modification, except with a total change of type. The part of the formula below the dotted line represents oxatyl, with cannot be altered without sacrificing the acid character of the compound; there remains therefore only the part of the formula above the dotted line, which admits of the following modification:—

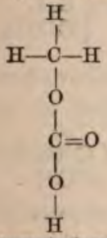


$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ O \\ | \\ \cdots\cdots \\ | \end{array}$$

The acid represented by the formula so modified no longer comes within the definition of the lactic series. It is carbomethylic acid, and differs essentially from glycollic acid and the lactic series in general, inasmuch as the carbon of its negative radical, oxatyl, is linked to the carbon of the positive radical by oxygen.*

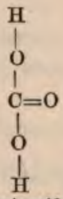
---

* Bearing this constitution of carbomethylic acid in mind, we have only to go one step further in order to perceive the constitution of carbonic acid itself, and the explanation of the anomalous basicity of this acid; for if, in the above graphic formula for carbomethylic acid, we replace the methyl by hydrogen, we have:—



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ O \\ | \\ C=O \\ | \\ O \\ | \\ H \end{array}$$

Carbomethylic acid.



$$\begin{array}{c} H \\ | \\ O \\ | \\ C=O \\ | \\ O \\ | \\ H \end{array}$$

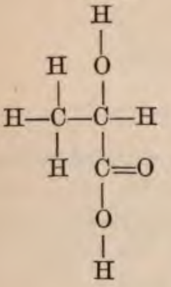
Carbonic acid.

It is thus evident that the radical oxatyl, when united with hydroxyl, has sufficient negative power to produce a feebly dibasic acid; but inasmuch as carbonic acid is not included in the category of organic acids, it forms no exception to the law that an organic acid containing *n* semimolecules of oxatyl is *n*-basic.

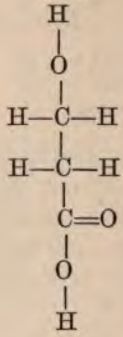
There being no decisive evidence that *homolactic acid* differs from glycollic acid, experiment and theory both agree in asserting that the formula $C_2H_4O_3$ represents only one acid in the lactic series.

Proceeding now one step higher in this series, we have in the formula of lactic acid an expression capable of the following three variations without quitting the lactic type:—

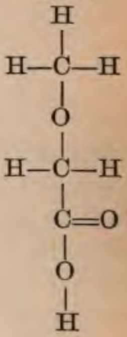
No. 1.



No. 2.



No. 3.

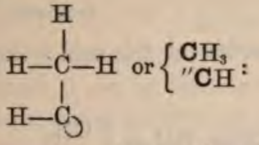


Or, expressed symbolically:—

No. 1. No. 2. No. 3.

$$\left\{\begin{array}{l}\mathbf{C}\text{MeHHo}\\ \mathbf{C}\text{OHo}\end{array}\right. . \quad \left\{\begin{array}{l}\mathbf{C}\text{H}_2\text{Ho}\\ \mathbf{C}\text{H}_2(\mathbf{C}\text{OHo})\end{array}\right. \text{ or} \left\{\begin{array}{l}\mathbf{C}\text{H}_2\text{Ho}\\ \mathbf{C}\text{H}_2\\ \mathbf{C}\text{OHo}\end{array}\right. . \quad \left\{\begin{array}{l}\mathbf{C}\text{H}_2\text{Meo}\\ \mathbf{C}\text{OHo}\end{array}\right. .$$

All the acids represented by the above formulæ are known. The first expresses the constitution of lactic acid, which belongs to the normal division $\left(\left\{\begin{array}{l}\mathbf{C}\overset{+}{\text{R}}\text{HHo}\\ \mathbf{C}\text{OHo}\end{array}\right.\right)$ of the series, described at page 166; the second shows the atomic arrangement of hydracrylic acid; whilst the third represents methylglycollic acid. The proof that the first two of these acids are so constituted is afforded by the synthetic processes sometimes employed to produce them; for ethylidenic cyanhydrate is converted by ebullition with potash into a salt of lactic acid, whilst ethylenic cyanhydrate is transformed under similar circumstances into hydracrylic acid. It has also been mentioned above, that hydracrylic acid is produced by the action of phosgene gas upon ethylene. Now the formation of ethylidene, or rather of its compounds, scarcely leaves a doubt that this body, if isolated, would have the following atomic constitution:—

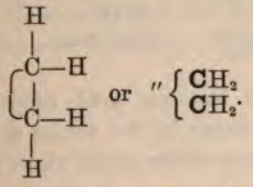


$$\begin{array}{rcl} & H & \\ & | & \\ H- & C & -H \\ & | & \\ H- & C & \circlearrowright \end{array} \text{ or } \left\{\begin{array}{l} CH_3 \\ {}''CH \end{array}\right. :$$

it would consist of a semimolecule of methyl and an atom of hydrogen, both united with an atom of carbon, two of the bonds of which satisfy each other. Thus the formation of ethylidenic chloride from aldehyde and phosphoric chloride takes place as follows:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{array}{l} CH_3 \\ CHO \end{array}\right.} + \underset{\text{Phosphoric chloride.}}{PCl_5} = \underset{\text{Ethylidenic chloride.}}{\left\{\begin{array}{l} CH_3 \\ CHCl_2 \end{array}\right.} + \underset{\text{Phosphoric oxytrichloride.}}{POCl_3},$$

the oxygen in the aldehyde being simply replaced by chlorine. There now only remains one possible formula for ethylene, viz.:—



$$\begin{array}{c} H \\ | \\ C-H \\ | \\ C-H \\ | \\ H \end{array} \text{ or } {}''\left\{\begin{array}{l} CH_2 \\ CH_2 \end{array}\right. .$$

Such, then, being the constitution of ethylidene and ethylene, it follows that the former ought to give rise to an acid of the constitution shown in formula No. 1, whilst ethylene should produce an acid agreeing with formula No. 2. The acids actually produced from these sources are lactic and hydracrylic acids; hence No. 1 is the constitutional formula of lactic acid, and No. 2 that of hydracrylic acid—a conclusion which harmonizes perfectly with all the reactions in which the production of these acids can be traced. Thus in the formation of lactic acid by the oxidation of propylic glycol, we have

$$\underset{\text{Propylic glycol.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{MeHHo}\\ \mathbf{C}\mathrm{H_2Ho}\end{matrix}\right.} + \mathrm{O_2} = \underset{\text{Lactic acid.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{MeHHo}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right.} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H_2}}.$$

Again, in the production of this acid from ethylidenic cyanhydrate,

$$\underset{\text{Ethylidenic cyanhydrate.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{HHo(CN''')}\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{\mathrm{KHo}} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H_2}} = \underset{\text{Potassic lactate.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{HHo(COKo)}\end{matrix}\right.} + \underset{\text{Ammonia.}}{\mathbf{N}\mathrm{H_3}}.$$

The formula given for potassic lactate in this equation is only apparently different in type from that previously used for lactic acid, since

$$\left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{HHo(COKo)}\end{matrix}\right. = \mathbf{C}\mathrm{MeHHo(COKo)} = \left\{\begin{matrix}\mathbf{C}\mathrm{MeHHo}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right..$$

In the reaction by which α-chloropropionic acid is transformed into lactic acid we have the following change:—

$$\underset{\alpha\text{-Chloropropionic acid.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{MeHCl}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{2\mathrm{KHo}} = \underset{\text{Potassic lactate.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{MeHHo}\\ \mathbf{C}\mathrm{OKo}\end{matrix}\right.} + \underset{\text{Potassic chloride.}}{\mathrm{KCl}} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H_2}}.$$

The production of lactamic acid (*alanin*), and that of lactic acid from the latter by the action of nitrous acid, are also clearly confirmatory of the above view.

$$\underset{\text{Ammonic aldehyde.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{H(NH_2)Ho}\end{matrix}\right.} + \underset{\text{Hydrocyanic acid.}}{\mathbf{N}\mathrm{CH}} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H_2}} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}} = \underset{\text{Lactamic acid (alanin).}}{\left\{\begin{matrix}\mathbf{C}\mathrm{MeH(N'''H_2)}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right.}$$

$$+ \underset{\text{Ammonic chloride.}}{\mathbf{N}\mathrm{H_4Cl}}:$$

$$\underset{\substack{\text{Lactamic acid}\\ \text{(alanin).}}}{\left\{\begin{array}{l}\mathrm{CMeH(N'''H_2)}\\ \mathrm{COHo}\end{array}\right.} + \underset{\substack{\text{Nitrous}\\ \text{acid.}}}{\mathrm{NOHo}} = \underset{\text{Lactic acid.}}{\left\{\begin{array}{l}\mathrm{CMeHHo}\\ \mathrm{COHo}\end{array}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}} + \mathrm{N_2}.$$

Not the least interesting reaction illustrative of the constitution of lactic acid is the formation of this acid by the action of nascent hydrogen upon pyruvic acid:—

$$\underset{\text{Pyruvic acid.}}{\left\{\begin{array}{l}\mathrm{COMe}\\ \mathrm{COHo}\end{array}\right.} + \mathrm{H_2} = \underset{\text{Lactic acid.}}{\left\{\begin{array}{l}\mathrm{CMeHHo}\\ \mathrm{COHo}\end{array}\right.}.$$

In a similar manner it can be demonstrated that the above formula No. 2 expresses the constitution of hydracrylic acid, which belongs to the fifth or olefine division of these acids,

$$\left\{\begin{array}{l}\overset{+}{\mathrm{C}}\mathrm{RHHo}\\ (\mathrm{CH_2})''_n(\mathrm{COHo})\end{array}\right. \text{ or } \left\{\begin{array}{l}\overset{+}{\mathrm{C}}\mathrm{RHHo}\\ (\mathrm{CH_2})''_n.\\ \mathrm{COHo}\end{array}\right.$$

That hydracrylic acid possesses this constitution is proved, first, by its production from cyanhydric glycol—

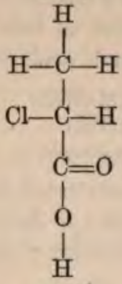
$$\underset{\substack{\text{Cyanhydric}\\ \text{glycol.}}}{\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CH_2(CN''')}\end{array}\right.} + \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{\mathrm{KHo}} + \underset{\text{Water.}}{\mathrm{OH_2}} = \underset{\substack{\text{Potassic}\\ \text{hydracrylate.}}}{\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CH_2}\\ \mathrm{COKo}\end{array}\right.} + \underset{\text{Ammonia.}}{\mathrm{NH_3}}$$

secondly, by its formation from phosgene gas and ethylene (see p. 172); and thirdly, by its conversion into malonic acid by the oxidizing action of dipotassic dichromate:—

$$\underset{\text{Hydracrylic acid.}}{\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.} + \mathrm{O_2} = \underset{\text{Malonic acid.}}{\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.} + \mathrm{OH_2}.$$

By the action of water upon the chloride of β-chlorpropionyl, a body of the composition of chloropropionic acid is obtained; but inasmuch as this body yields hydracrylic acid by ebullition with potash, whilst α-chloropropionic acid gives under the same circumstances lactic acid, it follows that the former chloro-acid must be isomeric, and not identical, with the latter. Now, although the formula of propionic acid does not admit of any isomer, yet that of chloropropionic acid does, as is seen in the following graphic formulæ:—

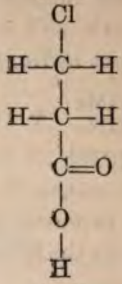
No. 1.



$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{Cl{-}C{-}H}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{O}\\ |\\ \mathrm{H}\end{array}$$

α-Acid.

No. 2.



$$\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{O}\\ |\\ \mathrm{H}\end{array}$$

β-Acid.

A comparison of these formulæ with those of lactic and hydracylic acids (p. 176) shows at a glance that No. 1 is the α-chloropropionic acid which yields lactic acid, whilst No. 2 is β-chloropropionic acid, which, by the substitution of its chlorine by hydroxyl, must yield hydracrylic acid. By the action of nascent hydrogen, both isomeric chlorides will obviously produce the same propionic acid.

The cause of the isomerism of methyl-glycollic acid (No. 3, p. 176) is so obvious as to require no further explanation. Proceeding to the next higher stage in the series, such is the rapid increase of isomeric forms, that we now encounter no less than eight possible isomers, all within the lactic family.

Normal.	Secondary.	Etheric normal.	
No. 1.	No. 2.	No. 3.	No. 4.
$\left\{\begin{array}{l}\mathrm{CEtHHo}\\ \mathrm{COHo}\end{array}\right.$.	$\left\{\begin{array}{l}\mathrm{CMe_2Ho}\\ \mathrm{COHo}\end{array}\right.$.	$\left\{\begin{array}{l}\mathrm{CH_2Eto}\\ \mathrm{COHo}\end{array}\right.$.	$\left\{\begin{array}{l}\mathrm{CMeHMeo}\\ \mathrm{COHo}\end{array}\right.$.

Normal olefine.			Etheric normal olefine.
No. 5.	No. 6.	No. 7.	No. 8.
$\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CH_2}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.$.	$\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CMeH}\\ \mathrm{COHo}\end{array}\right.$.	$\left\{\begin{array}{l}\mathrm{CMeHHo}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.$.	$\left\{\begin{array}{l}\mathrm{CH_2Meo}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.$.

Of these acids, Nos. 1, 2, 3, 5, and 7, are known. Nos. 1, 7, and 5, are α-, β-, and γ-oxybutyric acid; No. 2 is dimethoxalic acid, which is identical with acetonic acid. This being the case, the formation of the latter by the action of hydrocyanic and hydrochloric acids upon acetone is easily intelligible:—

$$\underset{\text{Acetone.}}{\left\{\begin{matrix}CH_3\\COMe\end{matrix}\right.} + \underset{\text{Hydrocyanic acid.}}{NCH} + \underset{\text{Water.}}{2OH_2} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Acetonic or dimethoxalic acid.}}{\left\{\begin{matrix}CMe_2Ho\\COHo\end{matrix}\right.} + NH_4Cl.$$

The third of the above formulæ is that of ethyl-glycollic acid.

Of the possible acids containing five atoms of carbon, only three, viz., ethomethoxalic acid, isovalerolactic acid, and α-methyl-β-oxybutyric acid, are known. The cause of the isomerism of these three acids is seen at once from an inspection of their constitutional formulæ:—

$$\text{Ethomethoxalic acid} \ldots\ldots\ldots \left\{\begin{matrix}CEtMeHo\\COHo\end{matrix}\right. .$$

$$\text{Isovalerolactic acid} \ldots\ldots\ldots \left\{\begin{matrix}CPrHHo\\COHo\end{matrix}\right. .$$

$$\alpha\text{-Methyl-}\beta\text{-oxybutyric acid} \ldots \left\{\begin{matrix}CMeHHo\\CMeH\\COHo\end{matrix}\right. .$$

Of acids containing six atoms of carbon, the following two are known:—

$$\text{Leucic acid} \ldots\ldots\ldots\ldots \left\{\begin{matrix}C\beta BuHHo^{*}\\COHo\end{matrix}\right.$$

$$\text{Diethoxalic acid} \ldots\ldots\ldots \left\{\begin{matrix}CEt_2Ho\\COHo\end{matrix}\right.$$

The above formula for leucic acid is founded upon a reaction for the synthetical production of amidocaproic acid from valeric aldehyde and hydrocyanic acid. Ordinary valeric acid contains isobutyl; consequently valeric aldehyde has the constitution expressed by the formula $\left\{\begin{matrix}\beta Bu\\ COH\end{matrix}\right.$; and the reaction in question is therefore explained by the following equation:—

---

* Perhaps $\left\{\begin{matrix}CBuHHo\\COHo\end{matrix}\right.$.

$$\underset{\text{Ammonic valeric aldehyde.}}{\left\{\begin{matrix}\beta Bu\\ CH(NH_2)Ho\end{matrix}\right.} + \underset{\text{Hydrocyanic acid.}}{NCH} + \underset{\text{Water.}}{OH_2} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Amidocaproic acid (leucin).}}{\left\{\begin{matrix}C\beta BuH(NH_2)\\ COHo\end{matrix}\right.}$$

$$+ \underset{\text{Ammonic chloride.}}{NH_4Cl}.$$

Such being the rational formula of amidocaproic acid, its transformation into leucic acid by nitrous acid determines the constitution of leucic acid:—

$$\underset{\text{Amidocaproic acid.}}{\left\{\begin{matrix}C\beta BuH(N'''H_2)\\ COHO\end{matrix}\right.} + \underset{\text{Nitrous acid.}}{NOHo} = \underset{\text{Leucic acid.}}{\left\{\begin{matrix}C\beta BuHHo\\ COHo\end{matrix}\right.} + \underset{\text{Water.}}{OH_2} + N_2.$$

It is not, however, quite certain that this leucin and leucic acid are identical with the naturally occurring leucin and the acid derived from it.

CHAPTER XIX.

THE ACIDS.

4. *PYRUVIC SERIES.*

General formula...... $\left\{\begin{matrix}CO(C_nH_{2n+1})\\ COHo\end{matrix}\right.$.

In this formula n may $= 0$, and the monad radical C_nH_{2n+1} may be replaced by other hydrocarbon monad radicals.

Only the following two members of this series are known:

Pyruvic acid	$\left\{\begin{matrix}COMe\\ COHo\end{matrix}\right.$.	Boils at 165°.
Benzoylformic acid	$\left\{\begin{matrix}COPh\\ COHo\end{matrix}\right.$.	Fuses at 65—66°.

Pyruvic acid is obtained by the destructive distillation of tartaric acid, and also by the action of aqueous hydrochloric acid on acetylic cyanide:—

$$\underset{\text{Acetylic cyanide.}}{\begin{cases}\mathrm{COMe}\\ \mathrm{CN}\end{cases}} + \underset{\text{Water.}}{2\mathrm{OH_2}} = \underset{\text{Pyruvic acid.}}{\begin{cases}\mathrm{COMe}\\ \mathrm{COHo}\end{cases}} + \underset{\text{Ammonia.}}{\mathrm{NH_3}}.$$

Benzoylformic acid is obtained in a similar manner from benzoylic cyanide, $\begin{cases}\mathrm{COPh}\\ \mathrm{CN}\end{cases}$.

The first member of this series would have the formula $\begin{cases}\mathrm{COH}\\ \mathrm{COHo}\end{cases}$. This acid is believed to be formed by the dehydration of glyoxylic acid; but its existence has not yet been satisfactorily demonstrated:—

$$\underset{\text{Glyoxylic acid.}}{\begin{cases}\mathrm{CHHo_2}\\ \mathrm{COHo}\end{cases}} - \mathrm{OH_2} = \underset{\text{Glyoxalic acid.}}{\begin{cases}\mathrm{COH}\\ \mathrm{COHo}\end{cases}}.$$

The aldehyde of this acid, however, is known. It is called glyoxal, and its formula is:—

$$\begin{cases}\mathrm{COH}\\ \mathrm{COH}\end{cases}.$$

Glyoxal is produced by the oxidation of ethylic alcohol by nitric acid:—

$$\underset{\text{Ethylic alcohol.}}{\begin{cases}\mathrm{CH_2}\\ \mathrm{CH_2Ho}\end{cases}} + 3\mathrm{O} = \underset{\text{Glyoxal.}}{\begin{cases}\mathrm{COH}\\ \mathrm{COH}\end{cases}} + \underset{\text{Water.}}{2\mathrm{OH_2}}.$$

These acids are the semi-ketones of oxalic acid, and they stand in much the same relation to this acid as that which acetone occupies with regard to acetic acid:—

$$\underset{\text{Acetic acid.}}{\begin{cases}\mathrm{CH_3}\\ \mathrm{COHo}\end{cases}} : \qquad \underset{\text{Acetone.}}{\begin{cases}\mathrm{CH_3}\\ \mathrm{COMe}\end{cases}}.$$

$$\underset{\text{Oxalic acid.}}{\begin{cases}\mathrm{COHo}\\ \mathrm{COHo}\end{cases}} : \qquad \underset{\text{Pyruvic acid.}}{\begin{cases}\mathrm{COMe}\\ \mathrm{COHo}\end{cases}}.$$

The pyruvic series is also closely related to the lacti series; pyruvic acid when treated with nascent hydrogen, is converted into normal lactic acid:—

$$\underset{\text{Pyruvic acid.}}{\left\{\begin{array}{l}\mathbf{C}OMe\\ \mathbf{C}OHo\end{array}\right.} + H_2 = \underset{\text{Lactic acid.}}{\left\{\begin{array}{l}\mathbf{C}MeHHo\\ \mathbf{C}OHo\end{array}\right.} .$$

5. *THE GLYOXYLIC SERIES OF ACIDS.*

$$\text{General formula..} \left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})Ho_2\\ \mathbf{C}OHo\end{array}\right. \text{or} \left\{\begin{array}{l}\mathbf{C}_nH_{2n}Ho\\ \mathbf{C}_mH_{2m-1}Ho.\\ \mathbf{C}OHo\end{array}\right.$$

In the second formula n may $= 0$.

The two following acids of this series are known:—

	Formula.	Physical condition.
Glyoxylic acid ..	$\left\{\begin{array}{l}\mathbf{C}HHo_2\\ \mathbf{C}OHo\end{array}\right.$.	Syrupy, crystalline hydrate.
Glyceric acid	$\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\\ \mathbf{C}OHo\end{array}\right.$.	Syrupy.

These acids are trihydric, but monobasic, and are related to the glycerin series of alcohols in the same way that the members of the lactic series are related to the glycols:—

$$\underset{\text{Glycol.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Ho\end{array}\right.} \qquad \underset{\text{Glycollic acid.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}OHo\end{array}\right.}$$

$$\underset{\text{Glycerin.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo.\\ \mathbf{C}H_2Ho\end{array}\right.} \qquad \underset{\text{Glyceric acid.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo.\\ \mathbf{C}OHo\end{array}\right.}$$

By a reaction similar to that which is believed to produce glyoxalic acid from glyoxylic acid, glyceric acid yields pyruvic acid:—

$$\underset{\text{Glyceric acid.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\\ \mathbf{C}OHo\end{array}\right.} - OH_2 = \underset{\text{Pyruvic acid.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}O\\ \mathbf{C}OHo\end{array}\right.} .$$

CHAPTER XX.

THE ACIDS.

6. *THE BENZOIC OR AROMATIC SERIES OF ACIDS.*

General formula.. $\left\{\begin{matrix} C_nH_{2n-7} \\ COHo \end{matrix}\right.$.

Formation.—1. By the oxidation of the aromatic or $C_nH_{2n-7}Ho$ alcohols:—

$$\underset{\text{Benzylic alcohol.}}{\left\{\begin{matrix} C_6H_5 \\ CH_2Ho \end{matrix}\right.} + O_2 = \underset{\text{Benzoic acid.}}{\left\{\begin{matrix} C_6H_5 \\ COHo \end{matrix}\right.} + OH_2.$$

2. By the oxidation of the aromatic aldehydes. Thus benzoic acid is formed from benzoic aldehyde, or oil of bitter almonds (see p. 140).

3. By the action of alkalies on the nitriles or abnormal cyanides. Thus potassic benzoate is formed by the action of potash upon benzonitrile:—

$$\underset{\text{Benzonitrile.}}{\left\{\begin{matrix} C_6H_5 \\ CN''' \end{matrix}\right.} + KHo + OH_2 = \underset{\text{Potassic benzoate.}}{\left\{\begin{matrix} C_6H_5 \\ COKo \end{matrix}\right.} + \underset{\text{Ammonia.}}{NH_3}.$$

4. By the action of sodium and carbonic anhydride on the bromides of the C_nH_{2n-7} radicals:—

$$\underset{\text{Phenylic bromide or monobrobenzol.}}{C_6H_5Br} + Na_2 + CO_2 = \underset{\text{Sodic benzoate.}}{\left\{\begin{matrix} C_6H_5 \\ CONao \end{matrix}\right.} + NaBr.$$

5. Some members of the series are produced by the oxidation of the hydrides of the C_nH_{2n-1} radicals:—

$$\underset{\text{Dimethyl-benzol.}}{C_6Me_2H_4} + 3O = \underset{\text{Toluic acid.}}{\left\{\begin{matrix} C_6MeH_4 \\ COHo \end{matrix}\right.} + OH_2.$$

6. The acids of the aromatic series may be obtained from the monamines of the series containing one atom less of carbon.

Thus phenylamine, when distilled with oxalic acid, produces phenylformamide:—

$$\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right. + \mathbf{N}H_2(C_6H_5) = \mathbf{N}H(C_6H_5)(CHO) + \mathbf{O}H_2 + \mathbf{C}O_2.$$

Oxalic acid. Phenylamine. Phenylformamide. Water. Carbonic anhydride.

Phenylformamide, by the action of heat, gives water and benzonitrile:—

$$\mathbf{N}H(C_6H_5)(CHO) \quad = \quad \mathbf{O}H_2 \quad + \quad \left\{\begin{matrix}\mathbf{C}_6H_5\\ \mathbf{C}N'''\end{matrix}\right..$$

Phenylformamide. Benzonitrile.

Benzonitrile, heated with potassic hydrate, gives potassic benzoate and ammonia:—

$$\left\{\begin{matrix}\mathbf{C}_6H_5\\ \mathbf{C}N'''\end{matrix}\right. \quad + \quad KHo \quad + \quad \mathbf{O}H_2 \quad + \quad \left\{\begin{matrix}\mathbf{C}_6H_5\\ \mathbf{C}OKo\end{matrix}\right. \quad + \quad \mathbf{N}H_3.$$

Benzonitrile. Potassic hydrate. Potassic benzoate. Ammonia.

Toluic acid, $\left\{\begin{matrix}\mathbf{C}_6H_4Me\\ \mathbf{C}OHo\end{matrix}\right.$, can thus be obtained from toluidine, $\mathbf{N}H_2(C_6H_4Me)$.

The following terms of this series are known:—

		Fusing-point.	Boiling-point.
Benzoic acid	$\left\{\begin{matrix}C_6H_5\\ COHo\end{matrix}\right.$	120°	250°
Orthotoluic acid	$\left\{\begin{matrix}C_6H_4Me\\ COHo\end{matrix}\right.$ (1 : 2)	102·5	—
Metatoluic acid	$\left\{\begin{matrix}C_6H_4Me\\ COHo\end{matrix}\right.$ (1 : 3)	109—110	—
Paratoluic acid	$\left\{\begin{matrix}C_6H_4Me\\ COHo\end{matrix}\right.$ (1 : 4)	180	275
Alphatoluic (phenylacetic) acid	$\left\{\begin{matrix}CPhH_2\\ COHo\end{matrix}\right.$	76·5	262
Mesitylenic acid	$\left\{\begin{matrix}C_6H_3Me_2\\ COHo\end{matrix}\right.$ (1 : 3 : 5)*	166	—
Xylic acid	$\left\{\begin{matrix}C_6H_3Me_2\\ COHo\end{matrix}\right.$ (1 : 2 : 4)*	126	—
Paraxylic acid	$\left\{\begin{matrix}C_6H_3Me_2\\ COHo\end{matrix}\right.$ (1 : 3 : 4)*	163	—

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* The semimolecule of oxatyl in the position 1.

		Fusing-point.	Boiling-point.
Alphaxylic acid............	$\left\{\begin{array}{l}C(C_6H_4Me)H_2\\COHo\end{array}\right.$ (1 : 4)	42°	—
Ethylbenzoic acid	$\left\{\begin{array}{l}C_6H_4Et\\COHo\end{array}\right.$ (1 : 4)	110	—
Hydrocinnamic (β-phenylpropionic) acid..............	$\left\{\begin{array}{l}CPhH_2\\CH_2\\COHo\end{array}\right.$	47·5	280°
Hydratropic (α-phenylpropionic) acid..............	$\left\{\begin{array}{l}CPhMeH\\COHo\end{array}\right.$	Liquid	265
Durylic acid	$\left\{\begin{array}{l}CH_2Me_3\\COHo\end{array}\right.$	150	—
Cuminic acid	$\left\{\begin{array}{l}C_6H_4\beta Pr\\COHo\end{array}\right.$ (1 : 4)	113	290

These acids have the same constitution as those of the acetic series, but contain the C_nH_{n-7} series of radicals. Other acids are also known holding towards the phenyl series the same relations as the acrylic, glycollic, pyruvic and glyoxylic series bear to the acetic series. The pyruvic acid of the phenyl series has already been referred to (p. 182). Cinnamic or β-phenylacrylic acid is an acryloid acid of this section, corresponding to β-phenylpropionic acid :—

$$\left\{\begin{array}{l}CPhH_2\\CH_2\\COHo\end{array}\right.$$

β-Phenylpropionic (hydrocinnamic) acid.

$$''\left\{\begin{array}{l}CPhH\\CH\\COHo\end{array}\right.$$

Cinnamic acid.

Cinnamic acid is decomposed, like the acids of the acrylic series, when heated with fused potassic hydrate; it gives under these circumstances potassic acetate and benzoate. For the analogous reaction in the acrylic series, see p. 162.

Atropic acid, obtained by the action of alkalies on atropine, has the formula, $\left\{\begin{array}{l}CPhMe''\\COHo\end{array}\right.$, and is isomeric with cinnamic acid.

Salicylic acid, oxybenzoic acid and paraoxybenzoic acid are the lactic acids of benzoic acid (see p. 189). The oil of meadow-sweet (*Spiræa ulmaria*) is the aldehyde of salicylic acid :—

$$\left\{\begin{matrix}C_6H_5Ho\\COH\end{matrix}\right. (1:2).$$

Anisic acid is paraoxybenzoic acid in which the phenylic hydroxyl has been replaced by methoxyl:—

$$\left\{\begin{matrix}C_6H_4Meo\\COHo\end{matrix}\right. (1:4).$$

Additional examples of the phenyllactic series are: five isomeric cresotic acids of the general formula, $\left\{\begin{matrix}C_6H_3MeHo\\COH\end{matrix}\right.$, further, oxymethyl-phenylformic acid, $\left\{\begin{matrix}C_6H_4(CH_2Ho)\\COHo\end{matrix}\right. (1:4)$, mandelic (phenylglycollic) acid, $\left\{\begin{matrix}CPhHHo\\COHo\end{matrix}\right.$, melilotic acid (from *Melilotus officinalis*), $\left\{\begin{matrix}CH_2(C_6H_4Ho)\\CH_2\\COHo\end{matrix}\right. (1:2)$, phloretic acid, $\left\{\begin{matrix}CMeH(C_6H_4Ho)\\COHo\end{matrix}\right. (1:4)$, and tropic acid,

$$\left\{\begin{matrix}CPhH(CH_2Ho)\\COHo\end{matrix}\right..$$

Numerous acids of the phenylglyoxylic series are known. One of these is protocatechuic acid, $\left\{\begin{matrix}C_6H_3Ho_2\\COHo\end{matrix}\right.$ (1 : 3 : 4, oxatyl in 1), metaparaoxybenzoic acid, some of the derivatives of which are well-known vegetable principles. *Vanillin*, the odoriferous principle of the vanilla bean, is protocatechuic aldehyde, in which the metahydroxyl-group has been replaced by methoxyl:—

$$C_6H_3(C\overset{1}{O}H)M\overset{3}{e}o\overset{4}{H}o$$

Vanillin
(metamethoxy-paraoxybenzoic aldehyde).

Vanillin is artificially prepared on a commercial scale from *coniferin*, $C_{16}H_{22}O_8$, a substance contained in the cambium of coniferous woods, such as the larch. When boiled with acids, coniferin takes up the elements of water, and is converted *into* coniferylic alcohol and glucose :—

$$\underset{\text{Coniferin.}}{C_{16}H_{22}O_8} + \underset{\text{Water.}}{OH_2} = \underset{\text{Coniferylic alcohol.}}{\left\{\begin{array}{l} C_6H_3MeoHo \\ C_3H_4Ho \end{array}\right.} + \underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

By oxidation with chromic acid, coniferylic alcohol yields vanillin:—

$$\underset{\text{Coniferylic alcohol.}}{\left\{\begin{array}{l} C_6H_3MeoHo \\ C_3H_4Ho \end{array}\right.} + 3O_2 = \underset{\text{Vanillin.}}{\left\{\begin{array}{l} C_6H_3MeoHo \\ COH \end{array}\right.} + \underset{\text{Carbonic anhydride.}}{2CO_2} + \underset{\text{Water.}}{2OH_2}.$$

Gallic acid, from gall-nuts, is a tetrahydric monobasic acid of the formula—

$$\left\{\begin{array}{l} C_6H_2Ho_3 \\ COHo \end{array}\right. .$$

It may therefore be regarded as benzoic acid, in which three atoms of hydrogen have been replaced by three semi-molecules of hydroxyl.

Tannic acid is obtained by the abstraction of one molecule of water from two molecules of gallic acid. Its constitutional formula is:—

$$\left\{\begin{array}{l} COHo \\ C_6H_2Ho_2 \\ O \\ C_6H_2Ho_2 \\ COHo \end{array}\right. .$$

BENZOIC ACID.

$$\left\{\begin{array}{l} C_6H_5 \\ COHo \end{array}\right. .$$

Molecular weight = 122. *Molecular volume* $\square\!\square$. 1 *litre of benzoic acid vapour weighs* 61 *criths. Fuses at* 120°. *Boils at* 250°.

Occurrence.—In many balsams and gums. In putrid urine.

Preparation.—1. By the oxidation of oil of bitter almonds (benzoic aldehyde, p. 140), cinnamic acid, styrolene, or any substitution derivative of benzene containing only one lateral carbon chain (see p. 61) :—

$$\underset{\text{Cinnamic acid.}}{''\left\{\begin{matrix}C(C_6H_5)H\\CH\\COHo\end{matrix}\right.} + 3O_2 = \underset{\text{Benzoic acid.}}{\left\{\begin{matrix}C_6H_5\\COHo\end{matrix}\right.} + \underset{\text{Carbonic anhydride.}}{2CO_2} + \underset{\text{Water.}}{OH_2.}$$

$$\underset{\text{Styrolene (phenylethylene).}}{''\left\{\begin{matrix}C(C_6H_5)H\\CH_2\end{matrix}\right.} + 5O = \underset{\text{Benzoic acid.}}{\left\{\begin{matrix}C_6H_5\\COHo\end{matrix}\right.} + \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Water.}}{OH_2.}$$

2. By the simultaneous action of sodium and carbonic anhydride on monobrombenzene :—

$$\underset{\text{Monobrom-benzene.}}{C_6H_5Br} + Na_2 + \underset{\text{Carbonic anhydride.}}{CO_2} = \underset{\text{Sodic benzoate.}}{\left\{\begin{matrix}C_6H_5\\CONao\end{matrix}\right.} + \underset{\text{Sodic bromide.}}{NaBr.}$$

3. By fusing together potassic benzenesulphonate and potassic formate :—

$$\underset{\text{Potassic benzene-sulphonate.}}{\left\{\begin{matrix}C_6H_5\\SO_2Ko\end{matrix}\right.} + \underset{\text{Potassic formate.}}{\left\{\begin{matrix}H\\COKo\end{matrix}\right.} = \underset{\text{Potassic benzoate.}}{\left\{\begin{matrix}C_6H_5\\COKo\end{matrix}\right.} + \underset{\text{Hydric potassic sulphite.}}{SOKoHo.}$$

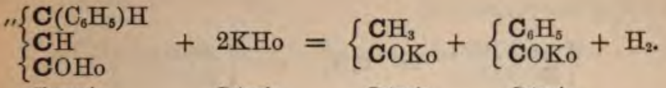
4. By heating benzotrichloride with water to 150° :—

$$\underset{\text{Benzotrichloride (phenylchloroform).}}{\left\{\begin{matrix}C_6H_5\\CCl_3\end{matrix}\right.} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Benzoic acid (phenylformic acid).}}{\left\{\begin{matrix}C_6H_5\\COHo\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{3HCl.}$$

5. By heating to a temperature of 330—350°, a mixture of two molecules of calcic phthalate with one molecule of calcic hydrate :—

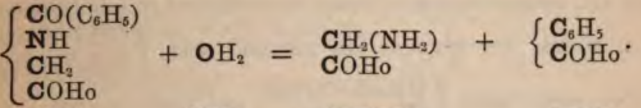
$$\underset{\text{Calcic phthalate.}}{2C_6H_4{\begin{matrix}CO\\CO\end{matrix}}Cao''} + \underset{\text{Calcic hydrate.}}{CaHo_2} = \underset{\text{Calcic benzoate.}}{\left\{\begin{matrix}C_6H_5\\CO\\CO\\C_6H_5\end{matrix}\right.{}^{}\!Cao''} + \underset{\text{Calcic carbonate.}}{2COCao''.}$$

6. By the action of fused potassic hydrate on cinnamic acid :—



$$\underset{\text{Cinnamic acid.}}{\left\{\begin{array}{l}\mathbf{C}(C_6H_5)H\\ \mathbf{C}H\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic acetate.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OKo\end{array}\right.} + \underset{\text{Potassic benzoate.}}{\left\{\begin{array}{l}\mathbf{C}_6H_5\\ \mathbf{C}OKo\end{array}\right.} + H_2.$$

7. By boiling hippuric acid (benzoylglycollamic acid) with hydrochloric acid :—



$$\underset{\text{Hippuric acid.}}{\left\{\begin{array}{l}\mathbf{C}O(C_6H_5)\\ \mathbf{N}H\\ \mathbf{C}H_2\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Glycollamic acid.}}{\begin{array}{l}\mathbf{C}H_2(NH_2)\\ \mathbf{C}OHo\end{array}} + \underset{\text{Benzoic acid.}}{\left\{\begin{array}{l}\mathbf{C}_6H_5\\ \mathbf{C}OHo\end{array}\right.}\cdot$$

8. By the action of oxidising agents on casein or gelatin.

9. From gum benzoin by sublimation, or by extraction with potassic hydrate, and subsequent precipitation of the acid by hydrochloric acid.

CHAPTER XXI.

THE ACIDS.

DIBASIC ACIDS.

$$\text{General formula.. } \mathbf{A}(COHo)_2 \text{ or } \left\{\begin{array}{l}\mathbf{A}(COHo)\\ \mathbf{B}(COHo)\end{array}\right.,$$

A and B being dyad radicals containing $C_nH_mO_l$.

These acids all contain two semimolecules of oxatyl; and if in the general formula n, m, and $l = 0$, oxalic acid will be the first term of the series.

Formation.—Many of the dibasic acids are produced by the oxidation of substances, the molecules of which are richer in carbon, such as oils and fats. Others are found ready formed in nature.

Reactions.—1. By the action of dehydrating substances, and even sometimes by heat alone, many of these acids lose water, forming anhydrides:—

$$\underset{\text{Acid.}}{\left\{\begin{matrix}\mathbf{A}(COHo)\\ \mathbf{B}(COHo)\end{matrix}\right.} = \underset{\text{Water.}}{\mathbf{O}H_2} + \underset{\text{Anhydride.}}{\left\{\begin{matrix}\mathbf{A}(CO\\ \mathbf{B}(CO\end{matrix}O\right)}.$$

The formation of anhydrides by the action of heat alone occurs most readily in the case of those dibasic acids in which the two semimolecules of oxatyl are attached to adjacent carbon atoms, for example, in succinic acid, $\left\{\begin{matrix}\mathbf{C}H_2(COHo)\\ \mathbf{C}H_2(COHo)\end{matrix}\right.$' pyrotartaric acid, $\left\{\begin{matrix}\mathbf{C}MeH(COHo)\\ \mathbf{C}H_2(COHo)\end{matrix}\right.$, and phthalic acid,

$$\mathbf{C}_6H_4(COHo)\ (1:2).$$

On the other hand, those dibasic acids in which the two semimolecules of oxatyl are united to the same carbon atom, as in malonic acid, $\mathbf{C}H_2(COHo)_2$, isosuccinic acid, $\mathbf{C}MeH(COHo)_2$, do not form anhydrides at all, but are decomposed by the action of heat into carbonic anhydride, and a monobasic acid:—

$$\underset{\substack{\text{Malonic}\\ \text{acid.}}}{\mathbf{C}H_2(COHo)_2} = \underset{\text{Acetic acid.}}{\mathbf{C}H_3(COHo)} + \underset{\substack{\text{Carbonic}\\ \text{anhydride.}}}{\mathbf{C}O_2}.$$

2. If the anhydride be submitted to the action of phosphoric chloride, an atom of oxygen is replaced by two of chlorine:—

$$\underset{\text{Anhydride.}}{\left\{\begin{matrix}\mathbf{A}(CO\\ \mathbf{B}(CO\end{matrix}O\right)} + \underset{\substack{\text{Phosphoric}\\ \text{chloride.}}}{\mathbf{P}Cl_5} = \underset{\text{Chloride.}}{\left\{\begin{matrix}\mathbf{A}(COCl)\\ \mathbf{B}(COCl)\end{matrix}\right.} + \underset{\substack{\text{Phosphoric}\\ \text{oxytrichloride.}}}{\mathbf{P}OCl_3}.$$

There are, however, some reactions which seem to indicate that these chlorides possess the formula, $\left\{\begin{matrix}\mathbf{A}(CCl_2\\ \mathbf{B}(CO\end{matrix}O\right)$.

3. Both the anhydrides and the chlorides are reconverted into the acids by the action of water:—

$$\underset{\text{Chloride.}}{\left\{\begin{matrix}A(COCl)\\B(COCl)\end{matrix}\right.} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Acid.}}{\left\{\begin{matrix}A(COHo)\\B(COHo)\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{2HCl.}$$

The dibasic acids may be divided into the four following series:—

1. Succinic or acetoid series .. $\left\{\begin{matrix}C_nH_{2n}(COHo)\\C_mH_{2m}(COHo)\end{matrix}\right.$.

In the first member of the series $m = 0$.

2. Fumaric or acryloid series.. ″ $\left\{\begin{matrix}C_nH_{2n-1}(COHo)\\C_nH_{2n-1}(COHo)\end{matrix}\right.$.
3. Malic or lactoid series ...... $\left\{\begin{matrix}C_nH_{2n-1}Ho(COHo)\\C_nH_{2n}(COHo)\end{matrix}\right.$.
4. Tartaric or glyoxyloid series. $\left\{\begin{matrix}C_nH_{2n-1}Ho(COHo)\\C_nH_{2n-1}Ho(COHo)\end{matrix}\right.$.

The first and second series are dibasic and *dihydric;* the third, dibasic and *trihydric;* and the fourth, dibasic and *tetrahydric.*

1. *THE SUCCINIC OR ACETOID SERIES.*

General formula.. $\left\{\begin{matrix}COHo\\C_nH_{2n}\\C_mH_{2m}\\COHo\end{matrix}\right.$ or $\left\{\begin{matrix}COHo\\C_nH_{2n}\\COHo\end{matrix}\right.$.

In addition to oxalic acid (oxatyl) which many chemists regard as the first member of this series, the following are some of the most important:—

		Fusing-point.
Malonic acid	$\left\{\begin{matrix}COHo\\CH_2\\COHo\end{matrix}\right.$	132°.
Succinic acid	$\left\{\begin{matrix}COHo\\CH_2\\CH_2\\COHo\end{matrix}\right.$	180
Isosuccinic acid	$\left\{\begin{matrix}COHo\\CMeH.\\COHo\end{matrix}\right.$	130

		Fusing-point.	
Pyrotartaric acid	$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}MeH\\ \mathbf{C}H_2\\ \mathbf{C}OHo\end{array}\right.$	112°	
Glutaric acid	$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}OHo\end{array}\right.$	97	Boils at 30
Adipic acid	$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}_4H_8\\ \mathbf{C}OHo\end{array}\right.$	148	
Pimelic acid	$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}_5H_{10}\\ \mathbf{C}OHo\end{array}\right.$	114	
Suberic acid	$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}_6H_{12}\\ \mathbf{C}OHo\end{array}\right.$	140	
Anchoic acid	$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}_7H_{14}\\ \mathbf{C}OHo\end{array}\right.$	106	
Sebacic acid	$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}_8H_{16}\\ \mathbf{C}OHo\end{array}\right.$	127	
Roccellic acid	$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}_{15}H_{30}\\ \mathbf{C}OHo\end{array}\right.$	132	

It is obvious that, with the exception of the first, there m
be several modifications of each of these acids. Thus, th
are two succinic acids, one containing ethylene, and the ot
ethylidene (see p. 177).

$$\left\{\begin{array}{l}\mathbf{C}H_2(COHo)\\ \mathbf{C}H_2(COHo)\end{array}\right. \text{ and } \left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H(COHo)_2\end{array}\right..$$

1. *Relations of the Succinic to the Lactic Series of Acids an the Glycols.*

These acids are related to the lactic series and to the glyc in the same way as the fatty acids are related to the monacid alcohols :—

$$\begin{array}{ccc} \left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Ho\end{matrix}\right. \cdot & \left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}OHo\end{matrix}\right. \cdot & \left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right. \cdot \\ \text{Glycol.} & \text{Glycollic acid.} & \text{Oxalic acid.} \end{array}$$

This relation, however, does not strictly extend beyond the first member, although it may be partially traced in the relations of malonic and adipic acid to paralactic and paraleucic acid :—

$$\begin{array}{ccc} \left\{\begin{matrix}\mathbf{C}H_2(\mathbf{C}H_2Ho)\\ \mathbf{C}H_2Ho\end{matrix}\right. \cdot & \left\{\begin{matrix}\mathbf{C}H_2(\mathbf{C}H_2Ho)\\ \mathbf{C}OHo\end{matrix}\right. \cdot & \left\{\begin{matrix}\mathbf{C}H_2(\mathbf{C}OHo)\\ \mathbf{C}OHo\end{matrix}\right. \\ \text{Propylic glycol.} & \text{Paralactic acid.} & \text{Malonic acid.} \\ \left\{\begin{matrix}\mathbf{C}_4H_8(\mathbf{C}H_2Ho)\\ \mathbf{C}H_2Ho\end{matrix}\right. \cdot & \left\{\begin{matrix}\mathbf{C}_4H_8(\mathbf{C}H_2Ho)\\ \mathbf{C}OHo\end{matrix}\right. \cdot & \left\{\begin{matrix}\mathbf{C}_4H_8(\mathbf{C}OHo)\\ \mathbf{C}OHo\end{matrix}\right. \cdot \\ \text{Unknown glycol.} & \text{Paraleucic acid.} & \text{Adipic acid.} \end{array}$$

2. *Relations of the Succinic Series to the Dyad Radicals.*

1. The acids of the succinic series are intimately related to the dyad radicals, the nitriles or abnormal cyanides of which are readily converted into dibasic acids by ebullition with potassic hydrate or hydrochloric acid :—

$$\begin{array}{ccccccccc} \left\{\begin{matrix}\mathbf{C}_nH_{2n}(CN''')\\ \mathbf{C}_nH_{2n}(CN''')\end{matrix}\right. & + & 2KHo & + & 2\mathbf{O}H_2 & = & \left\{\begin{matrix}\mathbf{C}_nH_{2n}(COKo)\\ \mathbf{C}_nH_{2n}(COKo)\end{matrix}\right. & + & 2\mathbf{N}H_3. \\ \text{Abnormal cyanide of the dyad radical.} & & \text{Potassic hydrate.} & & \text{Water.} & & \text{Potassic salt of the dibasic acid.} & & \text{Ammonia.} \end{array}$$

2. Some of these acids, when heated with excess of caustic baryta, give up two molecules of carbonic anhydride, yielding the hydrides of the dyad radicals :—

$$\begin{array}{ccccc} \left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}_6H_{12}\\ \mathbf{C}OHo\end{matrix}\right. & = & 2\mathbf{C}O_2 & + & (C_6H_{12})''H_2. \\ \text{Suberic acid.} & & \text{Carbonic anhydride.} & & \end{array}$$

$$\begin{array}{ccccc} \left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}_8H_{16}\\ \mathbf{C}OHo\end{matrix}\right. & = & 2\mathbf{C}O_2 & + & (C_8H_{16})''H_2. \\ \text{Sebacic acid.} & & \text{Carbonic anhydride.} & & \end{array}$$

These reactions are the analogues, in the dyad series, of the process by which marsh-gas is obtained from acetic acid. The hydrides of the dyad radicals so obtained are isomeric with those of the corresponding monad radicals.

The elimination of carbonic anhydride from a monobasic acid can only take place once, while from a dibasic acid it takes place in two successive stages:—

In the case of a monobasic acid,

$$\left\{\begin{matrix}C_nH_{2n+1}\\ COHo\end{matrix}\right. - CO_2 = C_nH_{2n+1}H.$$

In the case of a dibasic acid,

$$\text{1st stage..}\left\{\begin{matrix}C_nH_{2n}(COHo)\\ C_nH_{2n}(COHo)\end{matrix}\right. - CO_2 = \left\{\begin{matrix}C_nH_{2n+1}\\ C_nH_{2n}\\ COHo\end{matrix}\right. :$$

$$\text{2nd stage..}\left\{\begin{matrix}C_nH_{2n+1}\\ C_nH_{2n}\\ COHo\end{matrix}\right. - CO_2 = \left\{\begin{matrix}C_nH_{2n+1}\\ C_nH_{2n+1}\end{matrix}\right. .$$

3. *Relations of the Succinic to the Acetic Series of Acids.*

1. By the reducing action of hydriodic acid at 280°, succinic acid is converted into normal butyric acid:—

$$\underset{\text{Succinic acid.}}{\left\{\begin{matrix}CH_2(COHo)\\ CH_2(COHo)\end{matrix}\right.} + \underset{\text{Hydriodic acid.}}{6HI} = \underset{\text{Butyric acid.}}{\left\{\begin{matrix}CMeH_2\\ CH_2(COHo)\end{matrix}\right.} + \underset{\text{Water.}}{2OH_2} + 3I_2.$$

The reaction has been studied only in the case of butyric acid, but would probably extend to the other members of the series.

2. By the loss of the elements of carbonic anhydride, the first three members of the succinic series are converted into members of the acetic series, containing one atom of carbon less:—

$$\underset{\text{Oxalic acid.}}{\left\{\begin{matrix}COHo\\ COHo\end{matrix}\right.} = \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Formic acid.}}{\left\{\begin{matrix}H\\ COHo\end{matrix}\right.} .$$

$$\underset{\text{Malonic acid.}}{\left\{\begin{array}{l}COHo\\CH_2\\COHo\end{array}\right.} = \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Acetic acid.}}{\left\{\begin{array}{l}CH_3\\COHo\end{array}\right.} .$$

$$\underset{\text{Succinic acid.}}{\left\{\begin{array}{l}COHo\\C_2H_4\\COHo\end{array}\right.} = \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Propionic acid.}}{\left\{\begin{array}{l}CMeH_2\\COHo\end{array}\right.} .$$

In the first two cases the action of heat alone is sufficient to effect the transformation; but in the third the affinity of lime for carbonic anhydride must be superadded.

3. Conversely, the members of the acetic series may be converted into those of the succinic containing one atom of carbon more, by replacing one atom of the hydrogen in the positive radical of the acid by cyanogen, and then boiling with potassic hydrate:—

$$\underset{\text{Cyanacetic acid.}}{\left\{\begin{array}{l}CH_2(CN''')\\COHo\end{array}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic malonate.}}{\left\{\begin{array}{l}CH_2(COKo)\\COKo\end{array}\right.} + \underset{\text{Ammonia.}}{NH_3}.$$

The conversion of formic acid into oxalic acid, by heating with potassic hydrate, also belongs to this class of reactions:—

$$2\underset{\text{Formic acid.}}{\left\{\begin{array}{l}H\\COHo\end{array}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic oxalate.}}{\left\{\begin{array}{l}COKo\\COKo\end{array}\right.} + \underset{\text{Water.}}{2OH_2} + H_2.$$

SUCCINIC ACID.

$$\left\{\begin{array}{l}COHo\\CH_2\\CH_2\\COHo\end{array}\right. .$$

Fuses at 180°. *Dissolves in* 20 *parts of cold water.*

Occurrence.—In amber; in some kinds of lignite; in the resin of some kinds of pine; also in many other vegetable and in some animal substances.

Formation.—1. By the action of potassic hydrate upon abnormal ethylenic cyanide (p. 131): this reaction proves that succinic acid contains ethylene, and that its constitutional formula is as given above.

2. By the oxidation of butyric acid by nitric acid:—

$$\underset{\text{Butyric acid.}}{\left\{\begin{array}{l} CEtH_2 \\ COHo \end{array}\right.} + 3O = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l} COHo \\ C_2H_4 \\ COHo \end{array}\right.} + \underset{\text{Water.}}{OH_2}.$$

The nature of this reaction is more clearly seen with fully developed formulæ, thus:—

$$\underset{\text{Butyric acid.}}{\left\{\begin{array}{l} CH_3 \\ CH_2 \\ CH_2 \\ COHo \end{array}\right.} + 3O = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l} COHo \\ CH_2 \\ CH_2 \\ COHo \end{array}\right.} + \underset{\text{Water.}}{OH_2}.$$

3. By the reduction of malic acid by fermentation, or by hydriodic acid:—

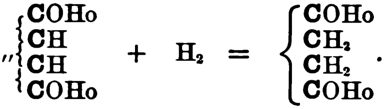
$$\underset{\text{Malic acid.}}{\left\{\begin{array}{l} COHo \\ CHHo \\ CH_2 \\ COHo \end{array}\right.} + H_2 = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l} COHo \\ CH_2 \\ CH_2 \\ COHo \end{array}\right.} + \underset{\text{Water.}}{OH_2}.$$

4. By the reduction of tartaric acid by hydriodic acid.

$$\underset{\text{Tartaric acid.}}{\left\{\begin{array}{l} COHo \\ CHHo \\ CHHo \\ COHo \end{array}\right.} + \underset{\text{Hydriodic acid.}}{4HI} = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l} COHo \\ CH_2 \\ CH_2 \\ COHo \end{array}\right.} + \underset{\text{Water.}}{2OH_2} + 2I_2.$$

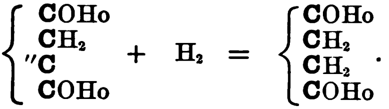
It is evident that this reaction is perfectly analogous to that by which lactic acid is transformed into propionic acid (p. 156).

5. The two isomeric acids, fumaric and maleic acids, are converted by nascent hydrogen into succinic acid:—



$$''\left\{\begin{array}{l}\mathrm{COHo}\\\mathrm{CH}\\\mathrm{CH}\\\mathrm{COHo}\end{array}\right. + \mathrm{H_2} = \left\{\begin{array}{l}\mathrm{COHo}\\\mathrm{CH_2}\\\mathrm{CH_2}\\\mathrm{COHo}\end{array}\right. .$$

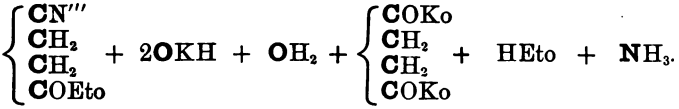
Succinic acid.



$$\left\{\begin{array}{l}\mathrm{COHo}\\\mathrm{CH_2}\\''\mathrm{C}\\\mathrm{COHo}\end{array}\right. + \mathrm{H_2} = \left\{\begin{array}{l}\mathrm{COHo}\\\mathrm{CH_2}\\\mathrm{CH_2}\\\mathrm{COHo}\end{array}\right. .$$

Succinic acid.

6. By boiling ethylic β-cyanopropionate with solution of caustic potash:—

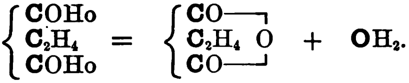


$$\left\{\begin{array}{l}\mathrm{CN}'''\\\mathrm{CH_2}\\\mathrm{CH_2}\\\mathrm{COEto}\end{array}\right. + 2\mathrm{OKH} + \mathrm{OH_2} + \left\{\begin{array}{l}\mathrm{COKo}\\\mathrm{CH_2}\\\mathrm{CH_2}\\\mathrm{COKo}\end{array}\right. + \mathrm{HEto} + \mathrm{NH_3}.$$

Ethylic β-cyanopropionate. Succinic acid. Alcohol. Ammonia.

The two processes by which succinic acid is generally prepared are, the distillation of amber and the fermentation of calcic malate.

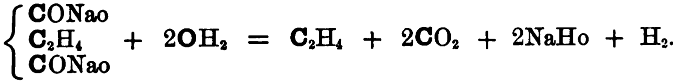
Reactions.—1 By distillation, succinic acid splits almost entirely into succinic anhydride and water:—



$$\left\{\begin{array}{l}\mathrm{COHo}\\\mathrm{C_2H_4}\\\mathrm{COHo}\end{array}\right. = \left\{\begin{array}{l}\mathrm{CO}—\\\mathrm{C_2H_4}\ \mathrm{O}\\\mathrm{CO}—\end{array}\right. + \mathrm{OH_2}.$$

Succinic acid. Succinic anhydride. Water.

2. On being submitted in solution to electrolysis, sodic succinate yields ethylene, carbonic anhydride, and sodium, the latter decomposing the water and forming sodic hydrate:—



$$\left\{\begin{array}{l}\mathrm{CONao}\\\mathrm{C_2H_4}\\\mathrm{CONao}\end{array}\right. + 2\mathrm{OH_2} = \mathrm{C_2H_4} + 2\mathrm{CO_2} + 2\mathrm{NaHo} + \mathrm{H_2}.$$

Succinic acid. Water. Ethylene. Carbonic anhydride.

3. Succinic acid may be boiled for hours with concentrated

nitric acid without suffering any change; neither is it affected by a mixture of potassic chlorate and hydrochloric acid; but it produces acetic acid when distilled with sulphuric acid and manganic oxide.

4. Succinic acid forms three kinds of salts, viz.:—

$$\begin{array}{cccc}
\text{Normal.} & \text{Acid.} & \multicolumn{2}{c}{\text{Superacid.}} \\
\left\{\begin{array}{l}\mathbf{C}\mathrm{OMo}\\ \mathbf{C}_2\mathrm{H}_4\\ \mathbf{C}\mathrm{OMo}\end{array}\right. . &
\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}_2\mathrm{H}_4\\ \mathbf{C}\mathrm{OMo}\end{array}\right. . &
\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}_2\mathrm{H}_4\\ \mathbf{C}\mathrm{OMo}\end{array}\right. , &
\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathrm{C}_2\mathrm{H}_4\\ \mathbf{C}\mathrm{OHo}\end{array}\right. .
\end{array}$$

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{O}—\\ \mathbf{C}_2\mathrm{H}_4\ \ \mathrm{Mo}''.\\ \mathbf{C}\mathrm{O}—\end{array}\right.$$

ISOSUCCINIC ACID.

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{MeH}.\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$$

Fuses at 130°. *Dissolves in* 5·4 *parts of cold water.*

Formation.—By boiling ethylic α-cyanopropionate with solution of caustic potash:—

$$\underset{\substack{\text{Ethylic}\\ \alpha\text{-cyanopropionate.}}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{N}'''\\ \mathbf{C}\mathrm{MeH}\\ \mathbf{C}\mathrm{OEto}\end{array}\right.} + 2\mathbf{O}\mathrm{KH} + \mathbf{O}\mathrm{H}_2 = \underset{\substack{\text{Potassic}\\ \text{isosuccinate.}}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{OKo}\\ \mathbf{C}\mathrm{MeH}\\ \mathbf{C}\mathrm{OKo}\end{array}\right.} + \underset{\text{Alcohol.}}{\mathrm{HEto}} + \underset{\text{Ammonia.}}{\mathbf{N}\mathrm{H}_3}.$$

CHAPTER XXII.

THE ACIDS.

2. *FUMARIC OR ACRYLOID SERIES.*

General formula.. $''\left\{\begin{array}{l}\mathbf{C}_n\mathrm{H}_{2n-1}(\mathbf{C}\mathrm{OHo})\\ \mathbf{C}_n\mathrm{H}_{2n-1}(\mathbf{C}\mathrm{OHo})\end{array}\right.$ or $\mathbf{C}_n\mathrm{H}_{2n-2}(\mathbf{C}\mathrm{OHo})_2$.

In this series there are two isomeric acids containing four atoms of carbon, viz.:—

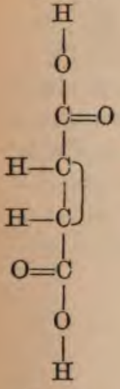
$$\left.\begin{array}{l}\text{Fumaric acid}\\ \text{Maleic acid}\end{array}\right\}\cdot\cdot\quad \overset{\text{Formula.}}{''\mathbf{C}''_2\mathrm{H}_2(\mathbf{C}\mathrm{OHo})_2};$$

and three other isomeric acids containing five atoms of carbon, viz. :—

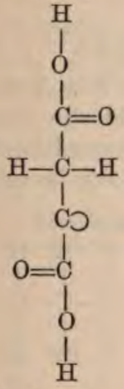
$$\left.\begin{array}{l}\text{Itaconic acid}\\ \text{Citraconic acid}\\ \text{Mesaconic acid}\end{array}\right\}\ldots\,{}^{vi}(\mathbf{C}_3)^{vi}H_4(COHo)_2.$$

Constitutional notation predicts the existence of four acids belonging to the four-carbon group. The following are the four possible formulæ for these acids :—

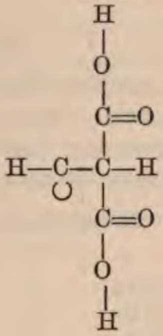
No. 1.



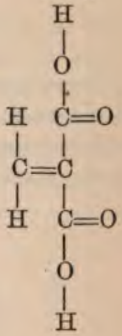
No. 2.



No. 3.



No. 4.



$''\left\{\begin{array}{l}\mathbf{COHo}\\ \mathbf{CH}\\ \mathbf{CH}\\ \mathbf{COHo}\end{array}\right. . \quad \left\{\begin{array}{l}\mathbf{COHo}\\ \mathbf{CH}_2\\ ''\mathbf{C}\\ \mathbf{COHo}\end{array}\right. . \quad \left\{\begin{array}{l}\mathbf{COHo}\\ \mathbf{C}(''\mathrm{CH})\mathrm{H}.\\ \mathbf{COHo}\end{array}\right. \quad \left\{\begin{array}{l}\mathbf{COHo}\\ \mathbf{C}\mathrm{Me}''.\\ \mathbf{COHo}\end{array}\right.$

Of these formulæ No. 1 is supposed to represent fumaric, and No. 2 maleic acid. Under the influence of nascent hydrogen both these acids yield succinic acid (see p. 198).

That succinic acid contains ethylene $\left(''\left\{\begin{array}{l}\mathbf{C}H_2\\ \mathbf{C}H_2\end{array}\right.\right)$ and not ethylidene $\left(\left\{\begin{array}{l}\mathbf{C}H_3\\ ''\mathbf{C}H\end{array}\right.\right)$, is proved by its formation from abnormal ethylenic cyanide (p. 131); but formulæ Nos. 3 and 4 give, by the addition of two atoms of hydrogen, the formula of isosuccinic acid containing ethylidene, thus :—

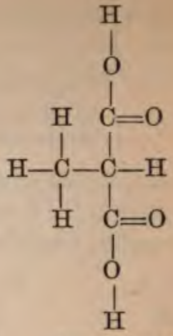
No. 3.

$$\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{C(''CH)H}\\ \mathrm{COHo}\end{array}\right. + \mathrm{H_2} = \left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CMeH}\\ \mathrm{COHo}\end{array}\right. .$$

No. 4.

$$\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CMe''}\\ \mathrm{COHo}\end{array}\right. + \mathrm{H_2} = \left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CMeH.}\\ \mathrm{COHo}\end{array}\right.$$

Isosuccinic acid.

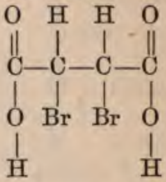


Isosuccinic acid.

Fumaric acid combines directly with bromine, producing dibromosuccinic acid. Maleic acid also combines directly with bromine, producing isodibromosuccinic acid. The following formulæ show the nature of this isomerism:—

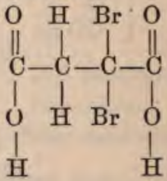
Corresponding to fumaric acid.

$$\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CHBr}\\ \mathrm{CHBr}\\ \mathrm{COHo}\end{array}\right.$$



Corresponding to maleic acid.

$$\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ \mathrm{CBr_2}\\ \mathrm{COHo}\end{array}\right.$$

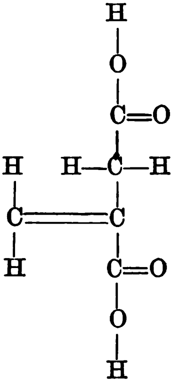


When acted upon by nascent hydrogen, both these isomeric bromo-acids produce, as might be expected, the same succinic acid:—

$$\underset{\text{Dibromsuccinic acid.}}{\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CHBr}\\ \mathrm{CHBr}\\ \mathrm{COHo}\end{array}\right.} + 2\mathrm{H}_2 = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH}_2\\ \mathrm{CH}_2\\ \mathrm{COHo}\end{array}\right.} + \underset{\text{Hydrobromic acid.}}{2\mathrm{HBr}}:$$

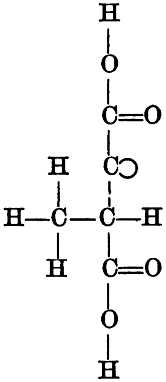
$$\underset{\text{Isodibromsuccinic acid.}}{\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH}_2\\ \mathrm{CBr}_2\\ \mathrm{COHo}\end{array}\right.} + 2\mathrm{H}_2 = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH}_2\\ \mathrm{CH}_2\\ \mathrm{COHo}\end{array}\right.} + \underset{\text{Hydrobromic acid.}}{2\mathrm{HBr}}.$$

Of a similar character is the relation subsisting between the isomeric acids of this series containing five atoms of carbon, viz., itaconic acid, citraconic acid, and mesaconic acid. There are no less than fourteen possible formulæ for this five-carbon group of acids; but the three individual formulæ belonging to the three known acids cannot at present be determined with certainty. It is supposed, however, that the formulæ of these three acids are—



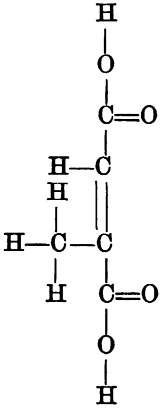
$$\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH}_2\\ \mathrm{CMe}''\\ \mathrm{COHo}\end{array}\right.$$

Itaconic acid.



$$\left\{\begin{array}{l}\mathrm{COHo}\\ ''\mathrm{C}\\ \mathrm{CMeH}\\ \mathrm{COHo}\end{array}\right.$$

Citraconic acid.

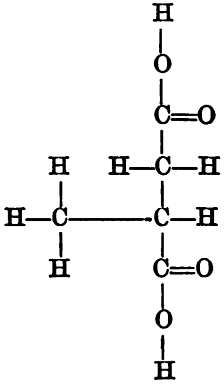


$$'' \left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH}\\ \mathrm{CMe}\\ \mathrm{COHo}\end{array}\right.$$

Mesaconic acid.

Itaconic, citraconic, and mesaconic acids stand in the same relation to pyrotartaric acid as fumaric and maleic acids occupy with regard to succinic acid; for, when submitted to the action of nascent hydrogen, they all yield the same pyrotartaric acid. The formula of pyrotartaric acid is

$$\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ \mathrm{CMeH}\\ \mathrm{COHo}\end{array}\right.$$



Treated with bromine, the three acids yield three isomeric brominated acids, which are transformed by nascent hydrogen into the same pyrotartaric acid.

By the action of bromine on itaconic acid and subsequent replacement of the bromine by hydroxyl, itatartaric acid is formed:—

$$\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ \mathrm{C(CH_2)''}\\ \mathrm{COHo}\end{array}\right. \qquad \left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ \mathrm{C(CH_2Br)Br}\\ \mathrm{COHo}\end{array}\right. \qquad \left\{\begin{array}{l}\mathrm{COHO}\\ \mathrm{CH_2}\\ \mathrm{C(CH_2Ho)Ho}\\ \mathrm{COHo}\end{array}\right.$$

Itaconic acid. Dibrompyrotartaric acid. Itatartaric acid.

CHAPTER XXIII.

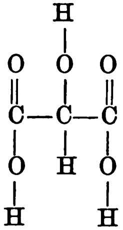
THE ACIDS.

3. *MALIC OR LACTOID SERIES.*

General formula.... $\left\{\begin{array}{l} C_nH_{2-1}Ho(COHo) \\ C_nH_{2n}(COHo) \end{array}\right.$ or $\left\{\begin{array}{l} COHo \\ C_nH_{2n-1}Ho. \\ COHo \end{array}\right.$

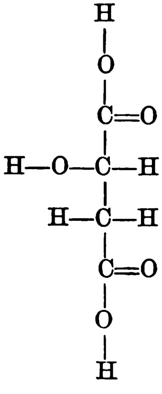
Several acids belonging to this series are known. The most important are tartronic acid and malic acid. Like lactic acid, they both contain a semimolecule of *non-oxatylic* hydroxyl:—

Tartronic acid.... $\left\{\begin{array}{l} COHo \\ CHHo. \\ COHo \end{array}\right.$



This acid may be regarded as the product of the oxidation of glycerin, although it has not yet been so produced. It is obtained by the gentle oxidation of tartaric acid (p. 208).

Malic acid ...... $\left\{\begin{array}{l} COHo \\ CHHo \\ CH_2 \\ COHo \end{array}\right.$



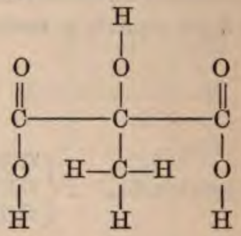
This acid is contained in apples and in many other fruits.

When gently heated with potassic hydrate, hydrogen is evolved, potassic oxalate and acetate being produced :—

$$\underset{\text{Potassic malate.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{OKo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{H_2}\\ \mathbf{C}\mathrm{OKo}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{\mathrm{KHo}} = \underset{\text{Potassic oxalate.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{OKo}\\ \mathbf{C}\mathrm{OKo}\end{array}\right.} + \underset{\text{Potassic acetate.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{OKo}\end{array}\right.} + \mathrm{H_2}.$$

Isomalic acid has the formula

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{MeHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$$



Isomalic acid may be viewed as the product of the oxidation of the hitherto undiscovered butyl glycerin $\left\{\begin{array}{l}\mathbf{C}\mathrm{H_2Ho}\\ \mathbf{C}\mathrm{MeHo}.\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.$

4. *TARTARIC OR GLYOXYLOID SERIES.*

This series contains at present only two members; but these have numerous isomers, which have been studied, however, only in the case of the first. Like the glyoxylic series, these acids contain two semimolecules of *non-oxatylic* hydroxyl.

Tartaric acid ...... $\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\cdot\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$

Itatartaric acid .... $\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{H_2}\\ \mathbf{C}\mathrm{(CH_2Ho)Ho}\cdot\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$

There are four varieties of tartaric acid known, viz.:—

1. Dextrotartaric or common tartaric acid, so called from its property of causing the plane of polarization of a ray of light to rotate to the right.

2. Lævotartaric acid, which turns the plane of polarization to the left.

3. Racemic acid, a compound of equal molecules of dextro- and lævotartaric acids. It is without action upon the polarized ray, its two opposite active constituents neutralizing each other. It may be produced artificially by the combination of dextro- and lævo-tartaric acid, and may again be resolved into them.

4. True inactive tartaric acid, which does not affect the plane of polarization and cannot be resolved into dextro- and lævo-tartaric acid.

All these varieties of tartaric acid possess the same constitutional formula:—

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right. \cdot$$

This is a case of what is known as "physical isomerism." The cause of this phenomenon has not been satisfactorily explained, although attempts have been made in this direction. A very important observation, however, apparently bearing directly upon this point, is that all organic compounds which act upon the plane of polarized light contain at least one so-called *asymmetric carbon atom*—a carbon atom united to four dissimilar atoms or groups. A very great number of these optically active compounds exhibit this physical isomerism—identity of chemical constitution coupled with difference of optical activity.

Dextrotartaric acid occurs in the juice of the grape.

By heating argentic dibromosuccinate with water a mixture of inactive tartaric acid and racemic acid is obtained:—

$$\underset{\text{Argentic dibromo-succinate.}}{\left\{\begin{array}{l}\mathrm{COAgo}\\\mathrm{CHBr}\\\mathrm{CHBr}\\\mathrm{COAgo}\end{array}\right.} + \underset{\text{Water.}}{2\mathrm{OH_2}} = \underset{\text{Inactive tartaric and racemic acid.}}{\left\{\begin{array}{l}\mathrm{COHo}\\\mathrm{CHHo}\\\mathrm{CHHo}\\\mathrm{COHo}\end{array}\right.} + \underset{\text{Argentic bromide.}}{2\mathrm{AgBr}}.$$

The racemic acid may be separated by crystallization. By heating the mother-liquor containing the inactive tartaric acid to 175° a portion of this acid is converted into racemic acid, which may again be separated as above. By a repetition of these processes the whole of the inactive acid may be transformed into racemic acid.

In order to resolve racemic acid into dextro- and lævo-tartaric acids, it is converted into sodic ammonic racemate,

$$\left\{\begin{array}{l}\mathrm{CONao}\\\mathrm{CHHo}\\\mathrm{CHHo}\\\mathrm{CO(NH_4O)}\end{array}\right. \cdot$$

The solution of this salt deposits two sets of crystals similar in all other respects, but differing in that one hemihedral* face is situated on the right hand in one set of crystals and on the left hand in the other. These crystals may be separated mechanically. The right-handed crystals yield dextrotartaric, the left-handed lævotartaric acid.

By heating ordinary dextrotartaric acid with water to 175° it is converted into a mixture of racemic and inactive tartaric acid.

Reactions.—1. Dextrotartaric acid, when treated with powerful oxidizing agents, gives formic acid.

2. Under the influence of very gentle oxidizing agents, tartronic acid is formed:—

$$\underset{\text{Tartaric acid.}}{\left\{\begin{array}{l}\mathrm{COHo}\\\mathrm{CHHo}\\\mathrm{CHHo}\\\mathrm{COHo}\end{array}\right.} + \mathrm{O_2} = \underset{\text{Tartronic acid.}}{\left\{\begin{array}{l}\mathrm{COHo}\\\mathrm{CHHo}\\\mathrm{COHo}\end{array}\right.} + \underset{\text{Carbonic anhydride.}}{\mathrm{CO_2}} + \underset{\text{Water.}}{\mathrm{OH_2}}$$

---

* Hemihedral faces are those which occur in only half their possible number.

3. By the action of hydriodic acid all the varieties of tartaric acid are converted into succinic acid (p. 198).

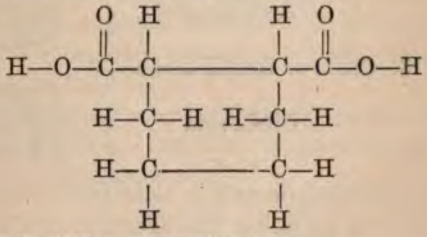
4. Heated with fused potassic hydrate, tartaric acid gives potassic oxalate and acetate, but without evolution of hydrogen:—

$$\underset{\text{Tartaric acid.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{3\mathrm{KHo}} = \underset{\text{Potassic oxalate.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{OKo}\\ \mathbf{C}\mathrm{OKo}\end{array}\right.} + \underset{\text{Potassic acetate.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{OKo}\end{array}\right.} + \underset{\text{Water.}}{3\mathbf{O}\mathrm{H_2}}.$$

OTHER SERIES OF DIBASIC ACIDS.

There is evidence of the existence of other series of dibasic acids, which may be regarded as derivatives of benzene or as the hexacarbon representatives of the succinic, fumaric, and tartaric series. The following are examples:—

$\mathbf{C}_6\mathrm{H}_{10}(\mathrm{COHo})_2$.

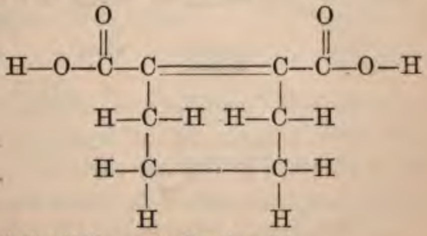


Hexahydrophthalic acid (Hexacarbon-succinic series).

$\mathbf{C}_6\mathrm{H}_8\mathrm{Ho}_2(\mathrm{COHo})_2$. (Relative position of the semimolecules of non-oxatylic hydroxyl unknown.)

Tartrophthalic acid (Hexacarbon-tartaric series).

$\mathbf{C}_6\mathrm{H}_8(\mathrm{COHo})_2$.



Tetrahydrophthalic acid (Hexacarbon-fumaric series).

CHAPTER XXIV.

THE ACIDS.

TRIBASIC ACIDS.

The tribasic acids all contain three semimolecules of oxatyl. They may be divided into the following three series, each series being, however, at present only represented by one acid.

1. Tricarballylic or acetoid series :—

$$\text{Tricarballylic acid} \ldots \left\{\begin{array}{l}\mathbf{C}\mathrm{H_2(COHo)}\\ \mathbf{C}\mathrm{H(COHo)}\\ \mathbf{C}\mathrm{H_2(COHo)}\end{array}\right. .$$

2. Aconitic or acryloid series :—

$$\text{Aconitic acid} \ldots\ldots \;{}^{\prime\prime}\left\{\begin{array}{l}\mathbf{C}\mathrm{H(COHo)}\\ \mathbf{C}\mathrm{(COHo)}\\ \mathbf{C}\mathrm{H_2(COHo)}\end{array}\right. .$$

3. Citric or lactoid series :—

$$\text{Citric acid} \ldots\ldots\ldots \left\{\begin{array}{l}\mathbf{C}\mathrm{H_2(COHo)}\\ \mathbf{C}\mathrm{Ho(COHo)}\\ \mathbf{C}\mathrm{H_2(COHo)}\end{array}\right. .$$

Tricarballylic acid is trihydric. It is obtained from glycerin by replacing the hydroxyl in the latter by cyanogen, and then acting upon the tricyanhydrin, so formed, by potassic hydrate :—

$$\underset{\text{Tricyanhydrin.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H_2(CN''')}\\ \mathbf{C}\mathrm{H(CN''')}\\ \mathbf{C}\mathrm{H_2(CN''')}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{3\mathrm{KHo}} + \underset{\text{Water.}}{3\mathbf{O}\mathrm{H_2}} = \underset{\text{Potassic tricarballylate.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H_2(COKo)}\\ \mathbf{C}\mathrm{H(COKo)}\\ \mathbf{C}\mathrm{H_2(COKo)}\end{array}\right.} + \underset{\text{Ammonia.}}{3\mathbf{N}\mathrm{H_3}}.$$

Aconitic acid (*equisetic acid*, *citridic acid*) is also trihydric. It is found in the roots and leaves of monkshood, and may also be obtained by heating citric acid. Aconitic acid is also produced by the action of hydrobromic acid upon citric acid, the reaction taking place in the two following stages :—

$$\underset{\text{Citric acid.}}{\left\{\begin{array}{l}CH_2(COHo)\\ CHo(COHo)\\ CH_2(COHo)\end{array}\right.} + HBr = \underset{\text{Bromotricarballylic acid.}}{\left\{\begin{array}{l}CH_2(COHo)\\ CBr(COHo)\\ CH_2(COHo)\end{array}\right.} + \underset{\text{Water.}}{OH_2};$$

$$\underset{\text{Bromotricarballylic acid.}}{\left\{\begin{array}{l}CH_2(COHo)\\ CBr(COHo)\\ CH_2(COHo)\end{array}\right.} = \underset{\text{Aconitic acid.}}{{}'' \begin{array}{l}\{CH(COHo)\\ \}C(COHo)\\ \{CH_2(COHo)\end{array}} + HBr.$$

Heated to 160°, aconitic acid is converted into itaconic acid:—

$$\underset{\text{Aconitic acid.}}{{}'' \begin{array}{l}\{CH(COHo)\\ \}C(COHo)\\ \{CH_2(COHo)\end{array}} = \underset{\text{Itaconic acid.}}{\left\{\begin{array}{l}COHo\\ CMe''\\ CH_2\\ COHo\end{array}\right.} + \underset{\text{Carbonic anhydride.}}{CO_2}.$$

Citric acid is tetrahydric, and contains, therefore, like lactic acid, one semimolecule of *non-oxatylic* hydroxyl. It is found in the free state in oranges, lemons, citrons, and many other fruits, also in the potato and the onion.

It has been prepared artificially by the following series of reactions. α-Dichlorhydrin, from glycerin, is converted by oxidation into symmetrical dichloracetone:—

$$\underset{\text{α-Dichlorhydrin.}}{\left\{\begin{array}{l}CH_2Cl\\ CHHo\\ CH_2Cl\end{array}\right.} + O = \underset{\text{Dichloracetone.}}{\left\{\begin{array}{l}CH_2Cl\\ CO\\ CH_2Cl\end{array}\right.} + \underset{\text{Water.}}{OH_2}.$$

Dichloracetone yields by treatment with concentrated hydrocyanic acid dichloracetone-cyanhydrate:—

$$\underset{\text{Dichloracetone.}}{\left\{\begin{array}{l}CH_2Cl\\ CO\\ CH_2Cl\end{array}\right.} + \underset{\text{Hydrocyanic acid.}}{CNH} = \underset{\text{Dichloracetone-cyanhydrate.}}{\left\{\begin{array}{l}CH_2Cl\\ CHo(CN).\\ CH_2Cl\end{array}\right.}$$

By the action of hydrochloric acid, the cyanogen group is converted into oxatyl, yielding the corresponding acid:—

$$\underset{\substack{\text{Dichloracetone}\\ \text{cyanhydrate.}}}{\left\{\begin{array}{l}CH_2Cl\\ CHo(CN)\\ CH_2Cl\end{array}\right.} + \underset{\text{Water.}}{2OH_2} = \underset{\substack{\text{Dichloroxy-}\\ \text{isobutyric acid.}}}{\left\{\begin{array}{l}CH_2Cl\\ CHo(COHo)\\ CH_2Cl\end{array}\right.} + \underset{\text{Ammonia.}}{NH_3}.$$

The potassium salt of this acid is then heated with a solution of potassic cyanide, by which means the chlorine is replaced by cyanogen :—

$$\underset{\substack{\text{Dichloroxy-}\\ \text{isobutyric acid.}}}{\left\{\begin{array}{l}CH_2Cl\\ CHo(COKo)\\ CH_2Cl\end{array}\right.} + \underset{\substack{\text{Potassic}\\ \text{cyanide.}}}{2K(CN)} = \underset{\substack{\text{Dicyanoxy-}\\ \text{butyric acid.}}}{\left\{\begin{array}{l}CH_2(CN)\\ CHo(COKo)\\ CH_2(CN)\end{array}\right.} + \underset{\substack{\text{Potassic}\\ \text{chloride.}}}{2KCl}.$$

This cyano-acid, when treated with hydrochloric acid, yields citric acid :—

$$\underset{\substack{\text{Dicyanoxy-}\\ \text{butyric acid.}}}{\left\{\begin{array}{l}CH_2(CN)\\ CHo(COHo)\\ CH_2(CN)\end{array}\right.} + \underset{\text{Water.}}{4OH_2} = \underset{\text{Citric acid.}}{\left\{\begin{array}{l}CH_2(COHo)\\ CHo(COHo)\\ CH_2(COHo)\end{array}\right.} + \underset{\text{Ammonia.}}{2NH_3}.$$

By the graduated application of heat, citric acid yields aconitic, itaconic, and citraconic acids. At the earlier stage of the decomposition it also yields acetone. Heated with fused potassic hydrate it gives potassic oxalate and acetate :—

$$\underset{\text{Citric acid.}}{\left\{\begin{array}{l}CH_2(COHo)\\ CHo(COHo)\\ CH_2(COHo)\end{array}\right.} + \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{4KHo} = \underset{\substack{\text{Potassic}\\ \text{oxalate.}}}{\left\{\begin{array}{l}COKo\\ COKo\end{array}\right.} + 2\underset{\substack{\text{Potassic}\\ \text{acetate.}}}{\left\{\begin{array}{l}CH_3\\ COKo\end{array}\right.} + \underset{\text{Water.}}{3OH_2}.$$

By being heated with hydriodic acid, citric acid is transformed into tricarballylic acid :—

$$\underset{\text{Citric acid.}}{\left\{\begin{array}{l}CH_2(COHo)\\ CHo(COHo)\\ CH_2(COHo)\end{array}\right.} + 2HI = \underset{\text{Tricarballylic acid.}}{\left\{\begin{array}{l}CH_2(COHo)\\ CH(COHo)\\ CH_2(COHo)\end{array}\right.} + \underset{\text{Water.}}{OH_2} + I_2.$$

Desoxalic acid is closely connected with citric acid; it is hexahydric, and may be regarded as citric acid in which two atoms of *non-oxatylic* hydrogen have been replaced by hydroxyl. Its constitutional formula is probably

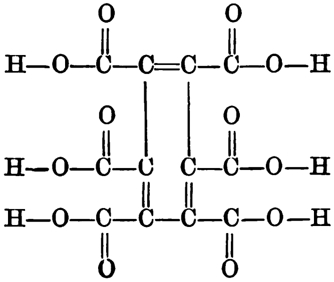
$$\left\{\begin{array}{l}\mathrm{CHHo(COHo)}\\ \mathrm{CHo(COHo)}\\ \mathrm{CHHo(COHo)}\end{array}\right. .$$

It is obtained from the product of the action of sodium upon oxalic ether.

TETRABASIC AND HEXABASIC ACIDS.

Pyromellitic acid ($C_6H_2(COHo)_4$) and *mellitic acid* ($C_6(COHo)_6$) are instances of acids of these degrees of basicity belonging to the benzene series; and it can scarcely be doubted that an intermediate pentabasic acid will be found to exist. It might be obtained by the oxidation of pentamethyl benzene, which has been prepared. The following graphic formula of mellitic acid shows the relation of this acid to benzene, and indicates the constitutional formulæ of the other acids built upon the same type and mentioned below :—

Mellitic acid.



Five out of the six possible acids thus related to benzene are now known. Their names and formulæ are given in the following table :—

Benzoic acid		$C_6H_5(COHo)$.
Phthalic acid (1 : 2)		$C_6H_4(COHo)_2$.
Isophthalic acid (1 : 3)		
Terephthalic acid (1 : 4)		
Trimellitic acid (1 : 2 : 4)		$C_6H_3(COHo)_3$.
Trimesic acid (1 : 3 : 5)		
Hemimellitic acid (1 : 2 : 3)		
Pyromellitic acid	(positions unknown)	$C_6H_2(COHo)_4$.
Prehnitic acid		
Mellophanic acid		
Unknown acid		$C_6H(COHo)_5$.
Mellitic acid		$C_6(COHo)_6$.

CHAPTER XXV.

THE ANHYDRIDES.

The anhydrides are compounds obtained from the acids by the abstraction of the hydrogen of their hydroxyl, together with sufficient oxygen to form water.

For every two atoms of hydrogen and one of oxygen thus abstracted from hydroxyl, there will obviously remain one atom of oxygen, which, as a dyad element, exactly satisfies the two bonds vacated by the hydroxyl:—

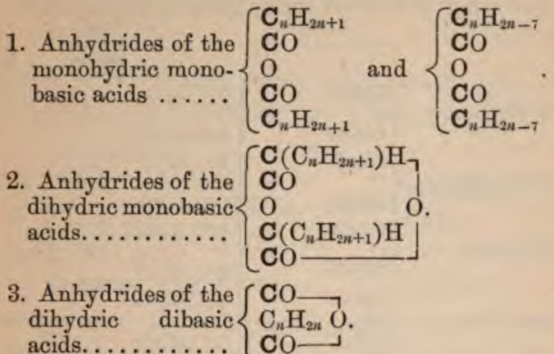
$$\underset{\text{Hydroxyl.}}{2Ho} = \underset{\text{Water.}}{OH_2} + O''.$$

On this account, two molecules of a monohydric acid are required to form one molecule of anhydride, thus:—

$$\underset{\text{Acetic acid.}}{2CMeOHo} = \underset{\text{Acetic anhydride.}}{\begin{cases} CMeO \\ O \\ CMeO \end{cases}} + \underset{\text{Water.}}{OH_2}.$$

The anhydrides of those monobasic and dibasic acids which contain one and two semimolecules of hydroxyl have alone been investigated.

They may be divided into the following classes :—



1. Anhydrides of the monohydric monobasic acids ......
$$\left\{\begin{array}{l}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}O\\ O\\ \mathbf{C}O\\ \mathbf{C}_nH_{2n+1}\end{array}\right. \quad \text{and} \quad \left\{\begin{array}{l}\mathbf{C}_nH_{2n-7}\\ \mathbf{C}O\\ O\\ \mathbf{C}O\\ \mathbf{C}_nH_{2n-7}\end{array}\right. .$$

2. Anhydrides of the dihydric monobasic acids............
$$\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})H\\ \mathbf{C}O\\ O \qquad\qquad O.\\ \mathbf{C}(C_nH_{2n+1})H\\ \mathbf{C}O\end{array}\right.$$

3. Anhydrides of the dihydric dibasic acids............
$$\left\{\begin{array}{l}\mathbf{C}O\\ C_nH_{2n}\ O.\\ \mathbf{C}O\end{array}\right.$$

1. *ANHYDRIDES OF THE MONOHYDRIC MONOBASIC ACIDS.*

These are known only in the acetic and benzoic series.

They bear the same relation to the acids from which they are derived as that borne by the ethers to the alcohols.

The residues of different acids unite to form mixed anhydrides analogous to the mixed ethers. Aceto-benzoic anhydride is a body of this class.

Formation.—By the action of the chloracids, or so-called chlorides of the monad negative radicals, on the potassic salts of the acids :—

$$\mathbf{C}(C_nH_{2n+1})OKo+\mathbf{C}(C_nH_{2n+1})OCl = \left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})O\\ O\\ \mathbf{C}(C_nH_{2n+1})O\end{array}\right. +KCl.$$

Potassic salt. Chloracid. Anhydride. Potassic chloride.

Reaction.—In contact with water they are converted into the corresponding acids :—

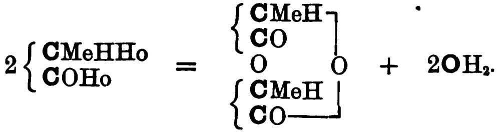
$$\underset{\text{Anhydride.}}{\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})O\\ O\\ \mathbf{C}(C_nH_{2n+1})O\end{matrix}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Acid.}}{2\mathbf{C}(C_nH_{2n+1})OHo.}$$

The following is a list of the anhydrides belonging to this class:—

		Fusing-point.	Boiling-point.
Acetic anhydride......	$\left\{\begin{matrix}\mathbf{C}MeO\\ O\\ \mathbf{C}MeO\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(CH_3)O\\ O\\ \mathbf{C}(CH_3)O\end{matrix}\right.$	—	138°
Propionic anhydride...	$\left\{\begin{matrix}\mathbf{C}EtO\\ O\\ \mathbf{C}EtO\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(C_2H_5)O\\ O\\ \mathbf{C}(C_2H_5)O\end{matrix}\right.$	—	165
Butyric anhydride.....	$\left\{\begin{matrix}\mathbf{C}PrO\\ O\\ \mathbf{C}PrO\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(C_3H_7)O\\ O\\ \mathbf{C}(C_3H_7)O\end{matrix}\right.$	—	about 190
Valeric anhydride	$\left\{\begin{matrix}\mathbf{C}BuO\\ O\\ \mathbf{C}BuO\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(C_4H_9)O\\ O\\ \mathbf{C}(C_4H_9)O\end{matrix}\right.$	—	about 215
Caproic anhydride.....	$\left\{\begin{matrix}\mathbf{C}AyO\\ O\\ \mathbf{C}AyO\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(C_5H_{11})O\\ O\\ \mathbf{C}(C_5H_{11})O\end{matrix}\right.$	—	—
Œnanthylic anhydride..	$\left\{\begin{matrix}\mathbf{C}CpO\\ O\\ \mathbf{C}CpO\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(C_6H_{13})O\\ O\\ \mathbf{C}(C_6H_{13})O\end{matrix}\right.$	42°	310
Benzoic anhydride.....	$\left\{\begin{matrix}\mathbf{C}(C_6H_5)O\\ O\\ \mathbf{C}(C_6H_5)O\end{matrix}\right.$	42	360
Acetobenzoic anhydride	$\left\{\begin{matrix}\mathbf{C}MeO\\ O\\ \mathbf{C}(C_6H_5)O\end{matrix}\right.$	—	—
Caprylic anhydride	$\left\{\begin{matrix}\mathbf{C}(C_7H_{15})O\\ O\\ \mathbf{C}(C_7H_{15})O\end{matrix}\right.$	below 0	about 290
Pelargonic anhydride ..	$\left\{\begin{matrix}\mathbf{C}(C_8H_{17})O\\ O\\ \mathbf{C}(C_8H_{17})O\end{matrix}\right.$	+5	—
Palmitic anhydride	$\left\{\begin{matrix}\mathbf{C}(C_{15}H_{31})O\\ O\\ \mathbf{C}(C_{15}H_{31})O\end{matrix}\right.$	53·8	—

3. *ANHYDRIDES OF THE DIHYDRIC MONOBASIC ACIDS.*

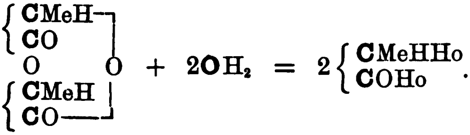
Formation.—By applying heat to a dihydric monobasic acid, thus:—



$$2\left\{\begin{array}{l}\mathrm{CMeHHo}\\ \mathrm{COHo}\end{array}\right. = \begin{array}{l}\left\{\begin{array}{l}\mathrm{CMeH}\\ \mathrm{CO}\end{array}\right.\\ \mathrm{O} \qquad \mathrm{O}\\ \left\{\begin{array}{l}\mathrm{CMeH}\\ \mathrm{CO}\end{array}\right.\end{array} + 2\mathrm{OH}_2.$$

Lactic acid. Lactide (Lactic anhydride). Water.

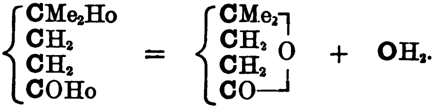
Reaction.—Boiled with water, and especially with alkalies, they reproduce the acids from which they were derived :—



$$\begin{array}{l}\left\{\begin{array}{l}\mathrm{CMeH}\\ \mathrm{CO}\end{array}\right.\\ \mathrm{O} \qquad \mathrm{O}\\ \left\{\begin{array}{l}\mathrm{CMeH}\\ \mathrm{CO}\end{array}\right.\end{array} + 2\mathrm{OH}_2 = 2\left\{\begin{array}{l}\mathrm{CMeHHo}\\ \mathrm{COHo}\end{array}\right. .$$

Lactide. Water. Lactic acid.

These anhydrides are formed from two molecules of acid and are known by the generic name of *lactides.* There is, however, a second class of anhydrides of the dihydric monobasic acids, formed from one molecule of acid, and known as *lactones.* As far as has yet been observed, it appears to be necessary to the formation of a *lactone*, that in the acid the semimolecules of oxatylic and non-oxatylic hydroxyl should be attached to two carbon atoms which are separated by two intermediate carbon atoms. An acid of this description does not seem to be capable of existing in the free state, for, as soon as it is liberated from its salts, it splits off the elements of water, yielding a lactone. This is the case with γ-oxycaproic acid :—



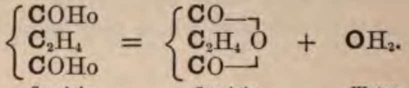
$$\left\{\begin{array}{l}\mathrm{CMe_2Ho}\\ \mathrm{CH_2}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right. = \left\{\begin{array}{l}\mathrm{CMe_2}\\ \mathrm{CH_2}\\ \mathrm{CH_2}\\ \mathrm{CO}\end{array}\right. \mathrm{O} + \mathrm{OH}_2.$$

γ-Oxycaproic acid. Lactone of γ-oxycaproic acid. Water.

The lactones are much more volatile than the lactides. They cannot be reconverted into their acids by boiling with water: for this purpose the action of caustic alkalies is necessary.

3. *ANHYDRIDES OF THE DIHYDRIC DIBASIC ACIDS.*

Formation.—By the action of heat, or of substances having a strong affinity for water, upon the dihydric dibasic acids (see p. 192):—



$$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}_2H_4\\ \mathbf{C}OHo\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}O-\\ \mathbf{C}_2H_4\,O\\ \mathbf{C}O-\end{array}\right. + \mathbf{O}H_2.$$

Succinic acid. Succinic anhydride. Water.

Reaction.—Like the anhydrides of the first and second classes, they unite with water, reproducing the acids from which they were derived.

CHAPTER XXVI.

THE KETONES.

The ketones are derived from the fatty acids by the substitution of the hydroxyl of the latter by a monad positive radical; they thus resemble the aldehydes in constitution:—

$$\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OHo\cdot\end{array}\right. \qquad \left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OH\cdot\end{array}\right. \qquad \left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OMe\cdot\end{array}\right.$$

Acetic acid. Acetic aldehyde. Acetone.

The ketones may also be correctly described as compounds of carbonic oxide with monad positive radicals, thus:—

$$\mathbf{C}OMe_2.$$

Acetone.

By the action of nascent hydrogen upon the ketones, they are converted into secondary alcohols, whilst the aldehydes, under the same treatment, yield normal alcohols:—

$$\underset{\text{Acetone.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{OMe}\end{array}\right.} + \mathrm{H}_2 = \underset{\text{Isopropylic alcohol.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{MeHHo}\end{array}\right.}$$

Ketones, unlike aldehydes, do not oxidize spontaneously; neither do they reduce ammoniacal solution of argentic oxide.

Like aldehydes, many of them combine with hydric potassic or hydric sodic sulphite. This reaction is confined to those ketones which contain at least one semimolecule of methyl directly united to the CO group.

Formation.—1. By the action of the zinc compounds of the positive monad radicals upon chloracids:—

$$2\underset{\text{Chloracid.}}{\left\{\begin{array}{l}\mathrm{C}_n\mathrm{H}_{2n+1}\\ \mathbf{C}\mathrm{OCl}\end{array}\right.} + \underset{\text{Zinc compound.}}{\mathbf{Zn}(\mathrm{C}_n\mathrm{H}_{2n+1})_2} = 2\underset{\text{Ketone.}}{\left\{\begin{array}{l}\mathrm{C}_n\mathrm{H}_{2n+1}\\ \mathbf{C}\mathrm{O}(\mathrm{C}_n\mathrm{H}_{2n+1})\end{array}\right.} + \underset{\text{Zincic chloride.}}{\mathbf{Zn}\mathrm{Cl}_2}.$$

2. By the action of sodic ethide and its homologues on carbonic oxide:—

$$\underset{\text{Carbonic oxide.}}{\mathbf{C}\mathrm{O}} + \underset{\text{Sodium compound.}}{2\mathrm{Na}(\mathrm{C}_n\mathrm{H}_{2n+1})} = \underset{\text{Ketone.}}{\left\{\begin{array}{l}\mathbf{C}_n\mathrm{H}_{2n+1}\\ \mathbf{C}\mathrm{O}(\mathrm{C}_n\mathrm{H}_{2n+1})\end{array}\right.} + \mathrm{Na}_2.$$

3. By the distillation of the salts of the fatty acids:—

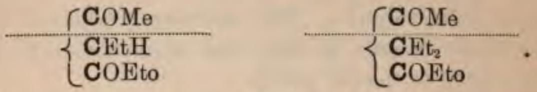
$$2\underset{\text{Potassic salt of fatty acid.}}{\left\{\begin{array}{l}\mathrm{C}_n\mathrm{H}_{2n+1}\\ \mathbf{C}\mathrm{OKo}\end{array}\right.} = \underset{\text{Ketone.}}{\left\{\begin{array}{l}\mathrm{C}_n\mathrm{H}_{2n+1}\\ \mathbf{C}\mathrm{O}(\mathrm{C}_n\mathrm{H}_{2n+1})\end{array}\right.} + \underset{\text{Potassic carbonate.}}{\mathbf{C}\mathrm{OKo}_2}.$$

4. By distilling together salts of two different fatty acids, ketones containing two different positive radicals are obtained:—

$$\underset{\text{Potassic butyrate.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{EtH}_2\\ \mathbf{C}\mathrm{OKo}\end{array}\right.} + \underset{\text{Potassic acetate.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{OKo}\end{array}\right.} = \underset{\text{Propylmethyl ketone.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{EtH}_2\\ \mathbf{C}\mathrm{OMe}\end{array}\right.} + \underset{\text{Potassic carbonate.}}{\mathbf{C}\mathrm{OKo}_2}.$$

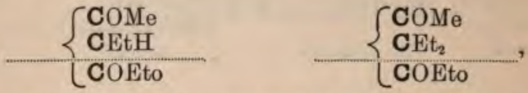
5. Numerous ketones may also be produced by the following series of reactions:—

It has been already mentioned (p. 151), that when treated with *concentrated* alcoholic potash, ethylic ethaceto-acetate yields a mixture of acetate and butyrate, whilst ethylic diethaceto-acetate is converted into a mixture of acetate and diethacetate. In this process, which is known as *acid saponification*, the separation of the carbon chain occurs chiefly at the point indicated by the dotted line:—



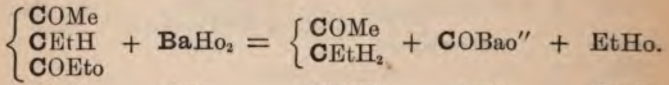
$$\left\{\begin{array}{l}\mathbf{C}\mathrm{OMe}\\ \hdashline \mathbf{C}\mathrm{EtH}\\ \mathbf{C}\mathrm{OEto}\end{array}\right. \qquad \left\{\begin{array}{l}\mathbf{C}\mathrm{OMe}\\ \hdashline \mathbf{C}\mathrm{Et_2}\\ \mathbf{C}\mathrm{OEto}\end{array}\right. .$$

If, however, an aqueous solution of baric hydrate be substituted for the alcoholic potash, the separation takes place thus:—



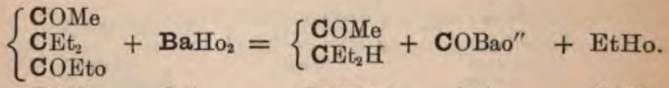
$$\left\{\begin{array}{l}\mathbf{C}\mathrm{OMe}\\ \mathbf{C}\mathrm{EtH}\\ \hdashline \mathbf{C}\mathrm{OEto}\end{array}\right. \qquad \left\{\begin{array}{l}\mathbf{C}\mathrm{OMe}\\ \mathbf{C}\mathrm{Et_2}\\ \hdashline \mathbf{C}\mathrm{OEto}\end{array}\right. ,$$

and a mixture of a ketone and a carbonate is the result. This process is termed *ketonic saponification*:—



$$\left\{\begin{array}{l}\mathbf{C}\mathrm{OMe}\\ \mathbf{C}\mathrm{EtH}\\ \mathbf{C}\mathrm{OEto}\end{array}\right. + \mathbf{Ba}\mathrm{Ho_2} = \left\{\begin{array}{l}\mathbf{C}\mathrm{OMe}\\ \mathbf{C}\mathrm{EtH_2}\end{array}\right. + \mathbf{C}\mathrm{OBao''} + \mathrm{EtHo}.$$

Ethylic ethaceto-acetate.	Baric hydrate.	Ethylated acetone.	Baric carbonate.	Ethylic alcohol.

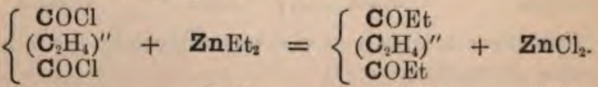


$$\left\{\begin{array}{l}\mathbf{C}\mathrm{OMe}\\ \mathbf{C}\mathrm{Et_2}\\ \mathbf{C}\mathrm{OEto}\end{array}\right. + \mathbf{Ba}\mathrm{Ho_2} = \left\{\begin{array}{l}\mathbf{C}\mathrm{OMe}\\ \mathbf{C}\mathrm{Et_2H}\end{array}\right. + \mathbf{C}\mathrm{OBao''} + \mathrm{EtHo}.$$

Ethylic diethaceto-acetate.	Baric hydrate.	Diethylated acetone.	Baric carbonate.	Ethylic alcohol.

6. By the action of zincic ethide on the chlorides obtained from the dibasic acids, ketones containing dyad radicals are produced; thus:—

Succinylic chloride submitted to the action of zincic ethide gives ethylene diethylic ketone:—



$$\left\{\begin{array}{l}\mathbf{C}\mathrm{OCl}\\ (\mathbf{C}_2\mathrm{H}_4)''\\ \mathbf{C}\mathrm{OCl}\end{array}\right. + \mathbf{Zn}\mathrm{Et_2} = \left\{\begin{array}{l}\mathbf{C}\mathrm{OEt}\\ (\mathbf{C}_2\mathrm{H}_4)''\\ \mathbf{C}\mathrm{OEt}\end{array}\right. + \mathbf{Zn}\mathrm{Cl_2}.$$

Succinylic chloride.	Zincic ethide.	Ethylene diethyl ketone.	Zincic chloride.

The following is a list of the names, constitutional formulæ, and boiling-points of those ketones which are best known :—

			Boiling-point.
	Acetone. (*Dimethyl ketone.*)	$\left\{\begin{matrix}CH_3\\ COMe\end{matrix}\right.$	56°
	Methylated acetone. (*Ethylmethyl ketone.*)	$\left\{\begin{matrix}CMeH_2\\ COMe\end{matrix}\right.$	81
Isomeric.	Dimethylated acetone.	$\left\{\begin{matrix}CMe_2H\\ COMe\end{matrix}\right.$	93·5
	Ethylated acetone	$\left\{\begin{matrix}CEtH_2\\ COMe\end{matrix}\right.$	101
	Propione. (*Diethyl ketone.*)	$\left\{\begin{matrix}CMeH_2\\ COEt\end{matrix}\right.$	101
Isomeric.	Methyl butyl ketone	$\left\{\begin{matrix}CPrH_2\\ COMe\end{matrix}\right.$	120
	Ethyl propyl ketone	$\left\{\begin{matrix}CEtH_2\\ COEt\end{matrix}\right.$	128
Isomeric.	Diethylated acetone	$\left\{\begin{matrix}CEt_2H\\ COMe\end{matrix}\right.$	138
	Bytyrone. (*Dipropyl ketone.*)	$\left\{\begin{matrix}CEtH_2\\ COPr\end{matrix}\right.$	144

The following are examples of the ketones of the C_nH_{2n-7} series :—

Benzophenone $\left(\left\{\begin{matrix}C_6H_5\\ CO(C_6H_5)\end{matrix}\right.\right)$, the ketone of benzoic acid, is obtained by heating potassic benzoate.

Methyl phenyl ketone or *acetophenone*,

$$\left(\left\{\begin{matrix}CH_3\\ CO(C_6H_5)\end{matrix}\right.\right),$$

is prepared by distilling together calcic acetate and benzoate.

Phthalylic chloride, treated with zincic ethide, produces *phenylene diethyl ketone* :—

$$\underset{\text{Phthalylic chloride.}}{\left\{\begin{matrix}COCl\\ (C_6H_4)''\\ COCl\end{matrix}\right.} + \underset{\text{Zincic ethide.}}{ZnEt_2} = \underset{\text{Phenylene diethyl ketone.}}{\left\{\begin{matrix}COEt\\ (C_6H_4)''\\ COEt\end{matrix}\right.} + \underset{\text{Zincic chloride.}}{ZnCl_2}.$$

CHAPTER XXVII.

ETHEREAL SALTS.

THESE compounds correspond to the metallic oxysalts of the acids.

The acids from which they are derived may be either mineral or organic; but the base must always be organic. The haloid ethereal salts are excluded from this family; they have been already described as haloid ethers.

The ethereal salts are produced by reactions analogous to those employed for the preparation of metallic salts:—

$$\underset{\text{Acetic acid.}}{\left\{\begin{matrix}CH_3\\COHo\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\substack{\text{Potassic}\\\text{acetate.}}}{\left\{\begin{matrix}CH_3\\COKo\end{matrix}\right.} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\text{Acetic acid.}}{\left\{\begin{matrix}CH_3\\COHo\end{matrix}\right.} + \underset{\substack{\text{Ethylic}\\\text{hydrate.}}}{EtHo} = \underset{\substack{\text{Ethylic}\\\text{acetate.}}}{\left\{\begin{matrix}CH_3\\COEto\end{matrix}\right.} + \underset{\text{Water.}}{OH_2}.$$

But as the hydrates of the organic radicals do not act upon acids so energetically as potassic hydrate, it is often advisable either to employ some dehydrating agent along with the mixture of alcohol and acid, or to resort to one of the following indirect methods:—

1. Action of a sulpho-acid of the radical upon an alkaline salt of the acid:—

$$\underset{\text{Sulpho-acid.}}{SO_2Ho(C_nH_{2n+1}O)} + \underset{\substack{\text{Potassic}\\\text{salt.}}}{\left\{\begin{matrix}C_mH_{2m+1}\\COKo\end{matrix}\right.} = \underset{\text{Ethereal salt.}}{\left\{\begin{matrix}C_mH_{2m+1}\\CO(C_nH_{2n+1}O)\end{matrix}\right.}$$

$$+ \underset{\substack{\text{Hydric potassic}\\\text{sulphate.}}}{SO_2HoKo}.$$

2. Action of a haloid ether of the radical upon an alkaline or silver salt of the acid:—

$$\underset{\text{Iodide of radical.}}{\mathbf{C}_nH_{2n+1}I} + \underset{\text{Silver salt.}}{\left\{\begin{array}{l}\mathbf{C}_mH_{2m+1}\\ \mathbf{C}OAgo\end{array}\right.} = \underset{\text{Ethereal salt.}}{\left\{\begin{array}{l}\mathbf{C}_mH_{2m+1}\\ \mathbf{C}O(C_nH_{2n+1}O)\end{array}\right.} + \underset{\text{Argentic iodide.}}{AgI.}$$

3. Action of the chloracids on the alcohols :—

$$\underset{\text{Alcohol.}}{\mathbf{C}_nH_{2n+1}Ho} + \underset{\text{Chloracid.}}{\left\{\begin{array}{l}\mathbf{C}_mH_{2m+1}\\ \mathbf{C}OCl\end{array}\right.} = \underset{\text{Ethereal salt.}}{\left\{\begin{array}{l}\mathbf{C}_mH_{2m+1}\\ \mathbf{C}O(C_nH_{2n+1}O)\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{HCl.}$$

4. By the action of the anhydrides of the acids on the alcohols :—

$$\underset{\text{Alcohol.}}{2\mathbf{C}_nH_{2n+1}Ho} + \underset{\text{Anhydride.}}{\left\{\begin{array}{l}\mathbf{C}(C_mH_{2m+1})O\\ O\\ \mathbf{C}(C_mH_{2m+1})O\end{array}\right.} = \underset{\text{Ethereal salt.}}{2\left\{\begin{array}{l}\mathbf{C}_mH_{2m+1}\\ \mathbf{C}O(C_nH_{2n+1}O)\end{array}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

This last reaction is greatly aided by the presence of a small quantity of zincic chloride, which acts as a dehydrating agent. In this form it is suited for the preparation of the ethereal salts of the polyhydric alcohols.

Monobasic acids form only one ethereal salt with each monohydric alcohol; and this salt is always normal.

With dihydric alcohols they each form two ethereal salts, and with trihydric alcohols three ethereal salts. These are also normal. Thus with acetic acid we have :—

Acetic salt of a monohydric alcohol :—

$$\underset{\text{Ethylic acetate.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OEto\cdot\end{array}\right.}$$

Acetic salts of a dihydric alcohol :—

$$\underset{\text{Monacetic glycol.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\cdot\end{array}\right.} \qquad \underset{\text{Diacetic glycol.}}{\left\{\begin{array}{l}\mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\cdot\end{array}\right.}$$

Acetic salts of a trihydric alcohol :—

$$\underset{\text{Monacetin.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\end{array}\right.} . \quad \underset{\text{Diacetin.}}{\left\{\begin{array}{l}\mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\\ \mathbf{C}HHo\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\end{array}\right.} . \quad \underset{\text{Triacetin.}}{\left\{\begin{array}{l}\mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\\ \mathbf{C}H\text{ -}O\text{-}\mathbf{C}MeO.\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\end{array}\right.}$$

Dibasic acids form, with monohydric alcohols, two series of ethereal salts:—

1. Acid ethereal salts, as:—

$$\text{Succinethylic acid} \ldots\ldots\ldots\ldots \left\{\begin{array}{l}\mathbf{C}\mathrm{OEto}\\ \mathbf{C}_2\mathrm{H}_4\\ \mathbf{C}\mathrm{OHo}\end{array}\right. .$$

2. Normal ethereal salts, as:—

$$\text{Ethylic succinate} \ldots\ldots\ldots\ldots \left\{\begin{array}{l}\mathbf{C}\mathrm{OEto}\\ \mathbf{C}_2\mathrm{H}_4\\ \mathbf{C}\mathrm{OEto}\end{array}\right. .$$

In the same manner, tribasic acids form with monohydric alcohols three series of ethereal salts, the first two of which are acid, and the third normal.

Prolonged contact with water generally decomposes ethereal salts, liberating the radicals of the bases in the form of alcohols:—

$$\underset{\substack{\text{Methylic}\\ \text{sulphomethylate.}}}{\mathbf{S}\mathrm{O}_2\mathrm{Meo}_2} + \underset{\text{Water.}}{2\mathbf{O}\mathrm{H}_2} = \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2} + \underset{\substack{\text{Methylic}\\ \text{alcohol.}}}{2\mathrm{MeHo}}.$$

Ebullition with potassic hydrate, especially when the latter is dissolved in alcohol, effects this transformation very speedily:—

$$\underset{\substack{\text{Ethylic}\\ \text{acetate.}}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{OEto}\end{array}\right.} + \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{\mathrm{KHo}} = \underset{\substack{\text{Potassic}\\ \text{acetate.}}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{OKo}\end{array}\right.} + \underset{\substack{\text{Ethylic}\\ \text{alcohol.}}}{\mathrm{EtHo}}.$$

CHAPTER XXVIII.

ORGANIC COMPOUNDS CONTAINING TRIAD AND PENTAD NITROGEN OR THEIR ANALOGUES.

THIS numerous family may be divided into two great classes:—

1. Compounds of triad nitrogen, phosphorus, arsenic, antimony, and bismuth.
2. Compounds of pentad nitrogen, phosphorus, arsenic, antimony, and bismuth.

I. *COMPOUNDS OF TRIAD NITROGEN AND OF ITS ANALOGUES.*

This class may be again subdivided as follows:—

Positive.	Neutral.	Negative.
1. Amines.	1. Amides.	1. Imides and nitrides of negative radicals.
2. Phosphines.	2. Alkalamides.	
3. Arsines.	3. Trichlorinated and tribrominated amines.	
4. Stibines.	4. Haloid compounds of oxybases.	
5. Bismuthines.		
6. Oxybases.		

Of these the Amines and Amides are the most important.

POSITIVE SECTION.

1. *THE AMINES.*

The Amines are commonly termed organic bases or artificial alkaloids; they are divided into—

A. Monamines.
B. Diamines.
C. Triamines.
D. Tetramines.

The tetramines have been but little investigated.

A. *MONAMINES.*

There are three kinds of monamines:—

α. Primary monamines.
β. Secondary monamines.
γ. Tertiary monamines.

α. *Primary Monamines.*

	General formulæ.
Methyl or C_nH_{2n+1} series......	$\mathbf{N}(C_nH_{2n+1})H_2$.
Allyl or C_nH_{2n-1} series	$\mathbf{N}(C_nH_{2n-1})H_2$.
Phenyl or C_nH_{2n-7} series	$\mathbf{N}(C_nH_{2n-7})H_2$.

Formation.—1. By the reduction of the nitro-substitution compounds of the hydrides of the positive radicals by sulphuretted hydrogen, ammonic sulphide, zinc and sulphuric acid, or iron and acetic acid:—

$$\underset{\text{Nitrobenzol.}}{\mathbf{N}(C_6H_5)O_2} + \underset{\text{Sulphuretted hydrogen.}}{3\mathbf{S}H_2} = \underset{\text{Aniline.}}{\mathbf{N}(C_6H_5)H_2} + \underset{\text{Water.}}{2\mathbf{O}H_2} + 3S.$$

2. By treating cyanic ethers with boiling solution of potassic hydrate. The reaction is perfectly analogous to the decomposition of cyanic acid with potassic hydrate:—

$$\underset{\text{Cyanic acid.}}{\mathbf{C}N'''Ho} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic carbonate.}}{\mathbf{C}OKo_2} + \underset{\text{Ammonia.}}{\mathbf{N}H_3}.$$

$$\underset{\text{Ethylic cyanate.}}{\mathbf{C}N'''Eto} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic carbonate.}}{\mathbf{C}OKo_2} + \underset{\text{Ethylamine.}}{\mathbf{N}EtH_2}.$$

3. By the action of the haloid compounds of the monad positive radicals upon ammonia, and subsequent action of potassic hydrate upon the product so formed:—

$$\underset{\text{Ammonia.}}{\mathbf{N}H_3} + \underset{\text{Ethylic iodide.}}{EtI} = \underset{\text{Ethylammonic iodide.}}{\mathbf{N}EtH_3I}.$$

$$\underset{\text{Ethylammonic iodide.}}{\mathbf{N}EtH_3I} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Ethylamine.}}{\mathbf{N}EtH_2} + \underset{\text{Potassic iodide.}}{KI} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

The following are a few of the primary monamines:—

Methylamine..........	$\mathbf{N}MeH_2$ or $\mathbf{N}(CH_3)H_2$.
Ethylamine	$\mathbf{N}EtH_2$ or $\mathbf{N}(C_2H_5)H_2$.
Butylamine	$\mathbf{N}BuH_2$ or $\mathbf{N}(C_4H_9)H_2$.
Amylamine	$\mathbf{N}AyH_2$ or $\mathbf{N}(C_5H_{11})H_2$.
Allylamine	$\mathbf{N}AllH_2$ or $\mathbf{N}(C_3H_5)H_2$.
Phenylamine (*Aniline*)	$\mathbf{N}PhH_2$ or $\mathbf{N}(C_6H_5)H_2$.
Tolylamine (*Toluidine*) three isomers, ortho, meta, and para.	$\mathbf{N}ToH_2$ or $\mathbf{N}(C_6H_4Me)H_2$.
Benzylamine	$\mathbf{N}BzH_2$ or $\mathbf{N}(CPhH_2)H_2$.

Reactions.—Treated with nitrous acid, they evolve nitrogen and yield the corresponding alcohols:—

$$\underset{\text{Ethylamine.}}{\mathbf{N}EtH_2} + \underset{\text{Nitrous acid.}}{\mathbf{N}OHo} = \underset{\substack{\text{Ethylic}\\\text{alcohol.}}}{EtHo} + N_2 + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

In the case of the amines of the phenyl series in which the nitrogen is directly united to the benzene nucleus, intermediate diazo-compounds are formed by the action of nitrous acid (see p. 68).

β. *Secondary Monamines.*

	General formulæ.
Methyl or C_nH_{2n+1} series	$\mathbf{N}(C_nH_{2n+1})_2H$.
Allyl or C_nH_{2n-1} series	$\mathbf{N}(C_nH_{2n-1})_2H$.
Phenyl or C_nH_{2n-7} series	$\mathbf{N}(C_nH_{2n-7})_2H$.

The secondary monamines are derived from ammonia by the replacement of two atoms of hydrogen by monad positive radicals. They are sometimes called *Imidogen bases.*

Formation.—By the action of the haloid compounds of the monad positive radicals on the primary monamines, and subsequent treatment with potassic hydrate:—

$$\underset{\text{Ethylamine.}}{\mathbf{N}EtH_2} + \underset{\substack{\text{Ethylic}\\\text{iodide.}}}{EtI} = \underset{\substack{\text{Diethylammonic}\\\text{iodide.}}}{\mathbf{N}Et_2H_2I}.$$

$$\underset{\substack{\text{Diethylammonic}\\\text{iodide.}}}{\mathbf{N}Et_2H_2I} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\text{Diethylamine.}}{\mathbf{N}Et_2H} + \underset{\substack{\text{Potassic}\\\text{iodide.}}}{KI} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

By using the iodide of a radical different from that already contained in the primary monamine, secondary monamines may be formed containing two different radicals, thus:—

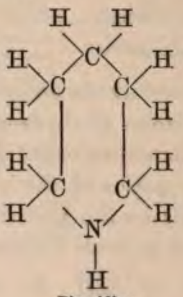
$$\underset{\substack{\text{Phenylamine.}\\\text{(Aniline.)}}}{\mathbf{N}PhH_2} + \underset{\substack{\text{Ethylic}\\\text{iodide.}}}{EtI} = \underset{\substack{\text{Ethylphenylammonic}\\\text{iodide.}}}{\mathbf{N}EtPhH_2I}.$$

$$\underset{\substack{\text{Ethylphenylam-}\\\text{monic iodide.}}}{\mathbf{N}EtPhH_2I} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\substack{\text{Ethylphenylamine.}\\\text{(Ethylaniline.)}}}{\mathbf{N}EtPhH} + \underset{\substack{\text{Potassic}\\\text{iodide.}}}{KI} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

The following are examples of secondary monamines :—

Dimethylamine	$\mathbf{N}\mathrm{Me}_2\mathrm{H}$	or $\mathbf{N}(\mathrm{CH}_3)_2\mathrm{H}$.
Diethylamine	$\mathbf{N}\mathrm{Et}_2\mathrm{H}$	or $\mathbf{N}(\mathrm{C}_2\mathrm{H}_5)_2\mathrm{H}$.
Diphenylamine	$\mathbf{N}\mathrm{Ph}_2\mathrm{H}$	or $\mathbf{N}(\mathrm{C}_6\mathrm{H}_5)_2\mathrm{H}$.
Methylethylamine	$\mathbf{N}\mathrm{MeEtH}$	or $\mathbf{N}(\mathrm{CH}_3)(\mathrm{C}_2\mathrm{H}_5)\mathrm{H}$.
Dibutylamine	$\mathbf{N}\mathrm{Bu}_2\mathrm{H}$	or $\mathbf{N}(\mathrm{C}_4\mathrm{H}_9)_2\mathrm{H}$.
Ethylamylamine	$\mathbf{N}\mathrm{EtAyH}$	or $\mathbf{N}(\mathrm{C}_2\mathrm{H}_5)(\mathrm{C}_5\mathrm{H}_{11})\mathrm{H}$.
Methylphenylamine	$\mathbf{N}\mathrm{MePhH}$	or $\mathbf{N}(\mathrm{CH}_3)(\mathrm{C}_6\mathrm{H}_5)\mathrm{H}$.
Ethylphenylamine	$\mathbf{N}\mathrm{EtPhH}$	or $\mathbf{N}(\mathrm{C}_2\mathrm{H}_5)(\mathrm{C}_6\mathrm{H}_5)\mathrm{H}$.
Piperidine		$\mathbf{N}(\mathrm{C}_5\mathrm{H}_{10})''\mathrm{H}$.
Conine		$\mathbf{N}(\mathrm{C}_8\mathrm{H}_{14})''\mathrm{H}$.

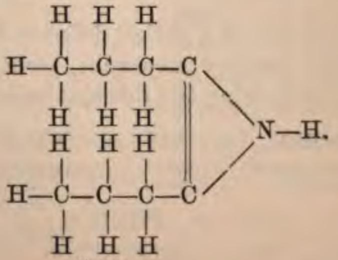
Piperidine is obtained from piperin, $\mathrm{C}_{17}\mathrm{H}_{19}\mathrm{NO}_3$, the active principle of pepper. It has the constitution—



Piperidine.

It yields on oxidation pyridine, $\mathbf{N}(\mathrm{C}_5\mathrm{H}_5)'''$ (see p. 231).

Conine is found in the juice of the hemlock (*Conium maculatum*). Its constitution is—



Conine.

It yields on oxidation butyric acid.

Reaction of Secondary Monamines.—With nitrous acid, the secondary monamines yield nitrosamines:—

$$\underset{\text{Diethylamine.}}{\mathbf{N}(C_2H_5)_2H} + \underset{\text{Nitrous acid.}}{\mathbf{N}OHo} = \underset{\text{Diethylnitrosamine.}}{\mathbf{N}(C_2H_5)_2(NO)} + \underset{\text{Water.}}{OH_2}$$

$$\underset{\text{Methylaniline.}}{\mathbf{N}MePhH} + \underset{\text{Nitrous acid.}}{\mathbf{N}OHo} = \underset{\text{Methylphenylnitrosamine.}}{\mathbf{N}MePh(NO)} + \underset{\text{Water.}}{OH_2}$$

γ. *Tertiary Monamines.*

Formation.—1. By acting upon the secondary monamines with the iodides of the monad positive radicals, and subsequently treating the product with potassic hydrate:—

$$\underset{\text{Diethylamine.}}{\mathbf{N}Et_2H} + \underset{\substack{\text{Ethylic}\\\text{iodide.}}}{EtI} = \underset{\substack{\text{Triethylammonic}\\\text{iodide.}}}{\mathbf{N}Et_3HI.}$$

$$\underset{\substack{\text{Triethylammonic}\\\text{iodide.}}}{\mathbf{N}Et_3HI} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\text{Triethylamine.}}{\mathbf{N}Et_3} + \underset{\substack{\text{Potassic}\\\text{iodide.}}}{KI} + \underset{\text{Water.}}{OH_2.}$$

By varying the radicals, tertiary monamines with several different radicals may be formed. The following are a few of the known tertiary monamines:—

Trimethylamine....	$\mathbf{N}Me_3$	or $\mathbf{N}(CH_3)_3$.
Triethylamine	$\mathbf{N}Et_3$	or $\mathbf{N}(C_2H_5)_3$.
Tributylamine	$\mathbf{N}Bu_3$	or $\mathbf{N}(C_4H_9)_3$.
Triamylamine......	$\mathbf{N}Ay_3$	or $\mathbf{N}(C_5H_{11})_3$.
Triphenylamine....	$\mathbf{N}Ph_3$	or $\mathbf{N}(C_6H_5)_3$.
Dimethylphenylamine	$\mathbf{N}Me_2Ph$	or $\mathbf{N}(CH_3)_2(C_6H_5)$.
Methyl-ethyl-phenylamine	$\mathbf{N}MeEtPh$	or $\mathbf{N}(CH_3)(C_2H_5)(C_6H_6)$.
Pyridine.........................		$\mathbf{N}(C_5H_5)'''$.
Picoline.........................		$\mathbf{N}(C_6H_7)'''$.
Lutidine.........................		$\mathbf{N}(C_7H_9)'''$.
Collidine.........................		$\mathbf{N}(C_8H_{11})'''$.
Parvoline		$\mathbf{N}(C_9H_{13})'''$.
Quinoline		$\mathbf{N}(C_9H_7)'''$.

2. When phenylammonic chloride (aniline hydrochlorate) and methylic alcohol are digested together at from 280° to 300°, the non-phenylic hydrogen becomes replaced by methyl, thus:—

$$\underset{\text{Phenylammonic chloride.}}{\mathbf{N}PhH_3Cl} + \underset{\text{Methylic alcohol.}}{MeHo} = \underset{\text{Methylphenylammonic chloride.}}{\mathbf{N}PhMeH_2Cl} + \mathbf{O}H_2.$$

$$\underset{\text{Methylphenylammonic chloride.}}{\mathbf{N}PhMeH_2Cl} + \underset{\text{Methylic alcohol.}}{MeHo} = \underset{\text{Dimethylphenylammonic chloride.}}{\mathbf{N}PhMe_2HCl} + \mathbf{O}H_2.$$

By continuing the digestion longer, the phenylic hydrogen is also replaced by methyl according to the following reaction:—

$$\underset{\text{Dimethylphenylammonic chloride.}}{\mathbf{N}(C_6H_5)Me_2HCl} + \underset{\text{Methylic alcohol.}}{MeHo} = \underset{\text{Dimethyltolylammonic chloride.}}{\mathbf{N}(C_6H_4Me)Me_2HCl} + \mathbf{O}H_2.$$

By these reactions the following tertiary monamines have been produced:—

Dimethylaniline	$\mathbf{N}(C_6H_5)Me_2$.
Dimethyltoluidine	$\mathbf{N}(C_6H_4Me)Me_2$.
Dimethylxylidine	$\mathbf{N}(C_6H_3Me_2)Me_2$.
Dimethylcumidine	$\mathbf{N}(C_6H_2Me_3)Me_2$.
Dimethylcymidine	$\mathbf{N}(C_6HMe_4)Me_2$.
Heptamethylaniline	$\mathbf{N}(C_6Me_5)Me_2$.

Tertiary monamines, when acted upon by the iodides of monad positive radicals, yield iodides which are not decomposed by potassic hydrate. In this manner tertiary monamines may be distinguished from primary and secondary monamines. The three may be distinguished from each other by the alternate action of ethylic iodide and potassic hydrate: thus, as we have just seen, tertiary monamines are recognized by producing immediately iodides which are not decomposed by potassic hydrate; a secondary monamine, however, produces an iodide decomposable by potassic hydrate; but the base thus liberated is tertiary, and will therefore be transformed immediately into the stable iodide by a second application of ethylic iodide. A primary monamine requires three applications of ethylic iodide and potassic hydrate to produce the same result.

Reaction.—1. When tertiary amines containing a semi-molecule of phenyl directly united to nitrogen are treated with nitrous acid, the nitroso-group (NO) replaces an atom of phenylic hydrogen:—

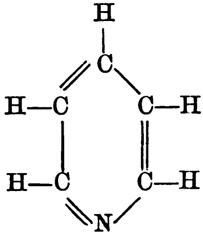
$$\underset{\text{Dimethylaniline.}}{\mathbf{N}(CH_3)_2(C_6H_5)} + \underset{\text{Nitrous acid.}}{\mathbf{N}OHo} = \underset{\text{Paranitroso-dimethyl-aniline.}}{\mathbf{N}(CH_3)_2[C_6H_4(NO)]} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

Paranitroso-dimethylaniline, when heated with dilute caustic soda, yields dimethylamine and a sodium salt of *paranitroso-phenol*:—

$$\underset{\text{Paranitroso-dimethyl-aniline.}}{\mathbf{N}(CH_3)_2[C_6H_4(NO)]} + \underset{\text{Sodic hydrate.}}{HNao} = \underset{\text{Dimethyl-amine.}}{\mathbf{N}(CH_3)_2H}$$

$$+ \underset{\text{Sodic para-nitroso-phenylate.}}{\mathbf{C}_6H_4(NO)Nao}.$$

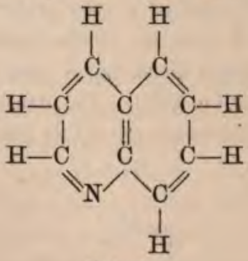
Pyridine Bases.—The five bases, pyridine, picoline, lutidine, collidine, and parvoline, are formed in the destructive distillation of nitrogenous organic matters. They occur in coal-tar, and in still larger quantity in bone oil. During the last few years they have acquired a very great interest, owing to the discovery that a number of the natural alkaloïds (see p. 242) are derived from these bases and from those of the allied quinoline series (p. 232). The constitution of pyridine is represented by the following graphic formula:—



Pyridine.

It is in fact benzene, in which one triad group, CH, has been replaced by N. Its relations to piperine have already been described (p. 228). On the assumption, already made in the case of benzene, that in a closed chain the influence of double and single bonds on the formation of isomers disappears (p. 53), it is evident that pyridine ought to yield three monosubstitution derivatives according as the replaced hydrogen atom is once, twice, or thrice removed from the nitrogen atom. As a fact three isomeric picolines, or methyl pyridines, are known, but the position of the methyl group in these three compounds has not been ascertained. It is probable that the higher homologues, lutidine, collidine, and parvoline, are di-, tri-, and tetra-methyl derivatives of pyridine, inasmuch as, on the analogy of the benzene series, no substitution compounds with substituted C_nH_{2n+1} radicals higher than methyl appear to be contained in coal-tar. The following are some of the natural alkaloids from which pyridine has been obtained: quinine, cinchonine, nicotine, and berberine (see p. 242).

Quinoline Bases.—Quinoline, $\mathbf{N}(C_9H_7)'''$, is formed when quinine, cinchonine, strychnine, and some other bases are distilled with potassic hydrate. It possesses the constitution—



Quinoline.

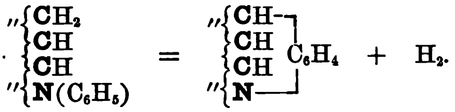
and stands in the same relation to pyridine as naphthalene to benzene (see pp. 64 and 71).

It may also be prepared in the following manner:—By the action of acroleïn on aniline, acroleïn-aniline is formed:—

$$''\left\{\begin{array}{l}\mathbf{CH_2}\\ \mathbf{CH}\\ \mathbf{COH}\end{array}\right. + \mathbf{N}(\mathrm{C_6H_5})\mathrm{H_2} = \begin{array}{l}''\left\{\begin{array}{l}\mathbf{CH_2}\\ \mathbf{CH}\end{array}\right.\\ ''\left\{\begin{array}{l}\mathbf{CH}\\ \mathbf{N}(\mathrm{C_6H_5})\end{array}\right.\end{array} + \mathrm{OH_2}.$$

Acroleïn. Aniline. Acroleïn-aniline. Water.

On distillation, acroleïn-aniline splits up into quinoline and hydrogen—

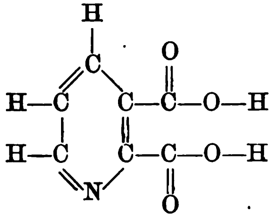


$$\begin{array}{l}''\left\{\begin{array}{l}\mathbf{CH_2}\\ \mathbf{CH}\end{array}\right.\\ ''\left\{\begin{array}{l}\mathbf{CH}\\ \mathbf{N}(\mathrm{C_6H_5})\end{array}\right.\end{array} = \begin{array}{l}''\left\{\begin{array}{l}\mathbf{CH}-\\ \mathbf{CH}\end{array}\right.\\ ''\left\{\begin{array}{l}\mathbf{CH}\\ \mathbf{N}-\end{array}\right.\end{array}\mathrm{C_6H_4} + \mathrm{H_2}.$$

Acrolein-aniline. Quinoline.

Other syntheses of quinoline are known, which leave no room for doubt as to its constitution.

On oxidation it yields dicarbopyridic acid—



Dicarbopyridic acid.

a reaction corresponding to the formation of phthalic acid from naphthalene (p. 71). And just as phthalic acid when distilled with excess of caustic lime yields benzene (p. 64), so dicarbopyridic acid yields under the same circumstances pyridine:—

$$\mathbf{N}[\mathrm{C_5H_3(COHo)_2}]''' + 2\mathrm{CaO} = \mathbf{N}(\mathrm{C_5H_5})''' + 2\mathrm{COCao}''.$$

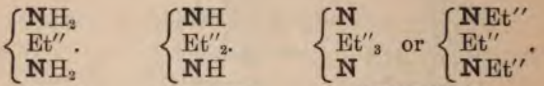
Dicarbopyridic acid. Lime. Pyridine. Calcic carbonate.

The following homologues of quinoline are known:—

Lepidine...............	$\mathbf{N}(\mathrm{C_{10}H_9})'''$.
Cryptidine............	$\mathbf{N}(\mathrm{C_{11}H_{11}})'''$.

B. *DIAMINES.*

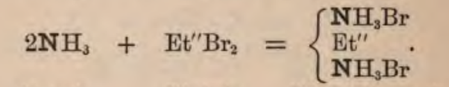
Formation.—The diamines are formed by coupling together two atoms of nitrogen in two molecules of ammonia, or of a primary or secondary monamine, by a dyad radical, which at the same time takes the place of two atoms of hydrogen; thus :—



$$\left\{\begin{matrix}\mathbf{N}H_2\\ Et''\\ \mathbf{N}H_2\end{matrix}\right. . \qquad \left\{\begin{matrix}\mathbf{N}H\\ Et''_2\\ \mathbf{N}H\end{matrix}\right. . \qquad \left\{\begin{matrix}\mathbf{N}\\ Et''_3\\ \mathbf{N}\end{matrix}\right. \text{ or } \left\{\begin{matrix}\mathbf{N}Et''\\ Et''\\ \mathbf{N}Et''\end{matrix}\right. .$$

Primary diamine. Secondary diamine. Tertiary diamine.

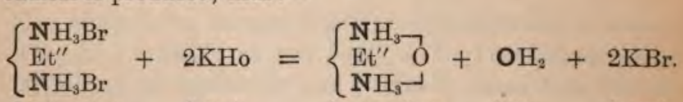
This reaction is effected by treating ammonia or a primary or secondary monamine with the haloid salt (preferably a bromide) of the dyad radical, thus :—



$$2\mathbf{N}H_3 + Et''Br_2 = \left\{\begin{matrix}\mathbf{N}H_3Br\\ Et''\\ \mathbf{N}H_3Br\end{matrix}\right. .$$

Ammonia. Ethylenic dibromide. Ethylene-diammonic dibromide.

When the salts of ethylene diammonium are decomposed by potassic hydrate, an oxide of the compound nitrogenous radical is produced, thus :—



$$\left\{\begin{matrix}\mathbf{N}H_3Br\\ Et''\\ \mathbf{N}H_3Br\end{matrix}\right. + 2KHo = \left\{\begin{matrix}\mathbf{N}H_3-\!\!\urcorner\\ Et''\ \ O\\ \mathbf{N}H_3-\!\!\lrcorner\end{matrix}\right. + \mathbf{O}H_2 + 2KBr.$$

Ethylene-diammonic dibromide. Potassic hydrate. Ethylene-diammonic oxide. Water. Potassic bromide.

In this respect most of the diamines differ from the monamines.

Urea and its derivatives belong to the class of diamines.

These compounds are produced by boiling a solution of ammonic cyanate or ethylammonic cyanate, or a homologue of the latter. In these compounds, the two atoms of nitrogen are held together by the dyad radical carbonyl, $\mathbf{CO}$:—

$$\begin{array}{ccc} CN'''(N^vH_4O) & = & \left\{\begin{matrix} NH_2 \\ CO \\ NH_2 \end{matrix}\right. . \\ \text{Ammonic cyanate.} & & \text{Urea.} \end{array}$$

$$\begin{array}{ccc} CN'''(N^vEtH_3O) & = & \left\{\begin{matrix} NHEt \\ CO \\ NH_2 \end{matrix}\right. . \\ \text{Ethyl-ammonic cyanate.} & & \text{Ethyl urea.} \end{array}$$

By heating ammonic carbonate to 130—140° in closed vessels for a few hours, urea is produced :—

$$\begin{array}{ccccc} CO(NH_4O)_2 & = & \left\{\begin{matrix} NH_2 \\ CO \\ NH_2 \end{matrix}\right. & + & 2OH_2. \\ \text{Ammonic carbonate.} & & \text{Urea.} & & \text{Water.} \end{array}$$

Ureas in which ethyl and other monad positive radicals are substituted for hydrogen may also be obtained by the action of ammonia or a monamine on the cyanic ethers, thus :—

$$\begin{array}{ccccc} CN'''Eto & + & NH_3 & = & \left\{\begin{matrix} NHEt \\ CO \\ NH_2 \end{matrix}\right. . \\ \text{Ethylic cyanate.} & & \text{Ammonia.} & & \text{Ethyl urea.} \end{array}$$

$$\begin{array}{ccccc} CN'''Eto & + & NH_2Et & = & \left\{\begin{matrix} NHEt \\ CO \\ NHEt \end{matrix}\right. . \\ \text{Ethylic cyanate.} & & \text{Ethylamine.} & & \text{Diethyl urea.} \end{array}$$

Reaction.—Urea is decomposed by nitrous anhydride :—

$$\begin{array}{ccccccccc} \left\{\begin{matrix} NH_2 \\ CO \\ NH_2 \end{matrix}\right. & + & N_2O_3 & = & CO_2 & + & 2N_2 & + & 2OH_2. \\ \text{Urea.} & & \text{Nitrous anhydride.} & & \text{Carbonic anhydride.} & & & & \text{Water.} \end{array}$$

The following is a list of the best known diamines :—

Ethylene diamine .... $\left\{\begin{matrix} NH_2 \\ Et'' \\ NH_2 \end{matrix}\right. .$

Ethylene diethyl diamine ...... $\left\{\begin{matrix}\mathbf{N}\mathrm{HEt}\\ \mathrm{Et}''\\ \mathbf{N}\mathrm{HEt}\end{matrix}\right.$.

Urea .... $\left\{\begin{matrix}\mathbf{N}\mathrm{H}_2\\ \mathbf{C}\mathrm{O}\\ \mathbf{N}\mathrm{H}_2\end{matrix}\right.$.

Sulphur urea .... $\left\{\begin{matrix}\mathbf{N}\mathrm{H}_2\\ \mathbf{C}\mathrm{S}''\\ \mathbf{N}\mathrm{H}_2\end{matrix}\right.$.

Ethyl urea .... $\left\{\begin{matrix}\mathbf{N}\mathrm{HEt}\\ \mathbf{C}\mathrm{O}\\ \mathbf{N}\mathrm{H}_2\end{matrix}\right.$.

Sulphophenylurea .... $\left\{\begin{matrix}\mathbf{N}\mathrm{HPh}\\ \mathbf{C}\mathrm{S}''\\ \mathbf{N}\mathrm{H}_2\end{matrix}\right.$.

Hydrazines.—The hydrazines are a peculiar class of diamines, in which the two atoms of nitrogen are directly united. They are derived from amidogen, $\left\{\begin{matrix}\mathbf{N}\mathrm{H}_2\\ \mathbf{N}\mathrm{H}_2\end{matrix}\right.$, by the substitution of a hydrocarbon radical for one or more of the hydrogen atoms, as in *phenylhydrazine*, $\left\{\begin{matrix}\mathbf{N}\mathrm{PhH}\\ \mathbf{N}\mathrm{H}_2\end{matrix}\right.$, *diethylhydrazine*, $\left\{\begin{matrix}\mathbf{N}\mathrm{Et}_2\\ \mathbf{N}\mathrm{H}_2\end{matrix}\right.$. Amidogen itself has not been prepared.

The primary hydrazines are obtained by acting on salts of diazo-compounds with an alkaline sulphite, and decomposing with hydrochloric acid the compound thus formed:—

$$\underset{\text{Diazobenzene nitrate.}}{\left\{\begin{matrix}\mathbf{N}\mathrm{Ph}\\ \mathbf{N}(\mathrm{ONO}_2)\end{matrix}\right.} + \underset{\text{Potassic sulphite.}}{2\mathbf{S}\mathrm{OKo}_2} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2} = \underset{\text{Potassic phenylhydrazine-sulphonate.}}{\left\{\begin{matrix}\mathbf{N}\mathrm{PhH}\\ \mathbf{N}\mathrm{H}(\mathrm{SO}_2\mathrm{Ko})\end{matrix}\right.}$$

$$+ \underset{\text{Potassic sulphate.}}{\mathbf{S}\mathrm{O}_2\mathrm{Ko}_2} + \underset{\text{Potassic nitrate.}}{\mathbf{N}\mathrm{O}_2\mathrm{Ko}}.$$

$$\underset{\text{Potassic phenylhydrazine sulphonate.}}{\left\{\begin{matrix}\mathbf{N}\mathrm{PhH}\\ \mathbf{N}\mathrm{H}(\mathrm{SO}_2\mathrm{Ko})\end{matrix}\right.} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}} = \underset{\text{Phenylhydrazonic chloride.}}{\left\{\begin{matrix}\mathbf{N}\mathrm{PhH}\\ \mathbf{N}\mathrm{H}_3\mathrm{Cl}\end{matrix}\right.} + \underset{\text{Hydric potassic sulphate.}}{\mathbf{S}\mathrm{O}_2\mathrm{HoKo}}.$$

By treating phenylhydrazonic chloride with an alkali, the free base is obtained.

Secondary hydrazines may be prepared by reducing the nitrosamines (p. 229) with zinc-dust and acetic acid :—

$$\underset{\text{Diethyl-nitrosamine.}}{\left\{\begin{matrix}\mathbf{N}\mathrm{Et}_2\\ \mathbf{N}\mathrm{O}\end{matrix}\right.} + 2\mathrm{H}_2 = \underset{\text{Diethyl-hydrazine.}}{\left\{\begin{matrix}\mathbf{N}\mathrm{Et}_2\\ \mathbf{N}\mathrm{H}_2\end{matrix}\right.} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2}.$$

C. *TRIAMINES.*

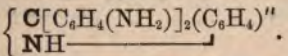
To this class of organic bases belong many of the aniline colours and their derivatives. *Mauveine* was the first discovered of these bodies; it is obtained by the action of concentrated sulphuric acid and red potassic chromate upon aniline. It is also produced by heating the coloured product obtained by the action of a solution of bleaching powder upon aniline. The molecular formula of mauveine is

$$N_4C_{26}H_{24}.$$

It is probably a tetramine, with the constitution shown in the following formula :—

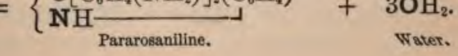
$$\mathbf{N}_4(C_7H_6)''_2(C_6H_4)''_2H_4.$$

A large and important class of colouring-matters is the *rosaniline group*, consisting of triamines derived from triphenylmethane (*triphenyl methylic hydride*, p. 96), $\mathbf{C}(C_6H_5)_3H$. The simplest member of this group is *pararosaniline*—



$$\left\{\begin{matrix}\mathbf{C}[C_6H_4(NH_2)]_2(C_6H_4)''\\ \mathbf{N}H\end{matrix}\right. .$$

Pararosaniline may be obtained by treating a mixture of one molecule of paratoluidine and two molecules of aniline with a weak oxidizing agent such as arsenic acid :—



$$\underset{\text{Paratoluidine.}}{\mathbf{C}_6H_4(CH_3)(NH_2)} + \underset{\text{Aniline.}}{2\mathbf{C}_6H_5(NH_2)} + 3O$$

$$= \underset{\text{Pararosaniline.}}{\left\{\begin{matrix}\mathbf{C}[C_6H_4(NH_2)]_2(C_6H_4)''\\ \mathbf{N}H\end{matrix}\right.} + \underset{\text{Water.}}{3\mathbf{O}H_2}.$$

It may also be prepared from triphenylmethane in a way which throws a clear light upon its constitution. Triphenylmethane yields with concentrated nitric acid (see p. 63) trinitrotriphenylmethane—

$$\mathbf{C}[C_6H_4(NO_2)_3]_3H,$$

which is converted by oxidation into trinitrotriphenyl carbinol—

$$\mathbf{C}[C_6H_4(NO_2)_3]_3Ho.$$

When this compound is subjected to the action of nascent hydrogen (from zinc and acetic acid), the nitro-groups are replaced by amidogen (p. 63), yielding triamidotriphenyl carbinol—

$$\mathbf{C}[C_6H_4(NH_2)]_3Ho.$$

This substance, however, at the moment of its formation spontaneously parts with the elements of water—the semimolecule of hydroxyl being eliminated along with one atom of amidic hydrogen—and forms pararosaniline:—

$$\underset{\substack{\text{Triamidotriphenyl}\\ \text{carbinol.}}}{\mathbf{C}[C_6H_4(NH_2)]_3Ho} - \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Pararosaniline.}}{\left\{\begin{array}{l}\mathbf{C}[C_6H_4(NH_2)]_2(C_6H_4)'' \\ \mathbf{N}H\text{—————————}\rfloor\end{array}\right.}.$$

A third method of preparing pararosaniline consists in heating aniline with carbonic chloride:—

$$\underset{\substack{\text{Carbonic}\\ \text{chloride.}}}{\mathbf{C}Cl_4} + \underset{\text{Aniline.}}{3\mathbf{C}_6H_5(NH_2)} = \underset{\text{Pararosaniline.}}{\left\{\begin{array}{l}\mathbf{C}[C_6H_4(NH_2)]_2(C_6H_4)'' \\ \mathbf{N}H\text{—————————}\rfloor\end{array}\right.} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{4HCl.}$$

Ordinary rosaniline, the base of the colouring matter magenta, is prepared by the action of arsenic acid on a mixture of two molecules of toluidine with one of aniline. It has the same constitution as pararosaniline, one of the phenylene groups of the latter being, however, replaced by tolylene, $(C_7H_6)'' = (C_6H_3Me)''$:—

$$\underset{\text{Pararosaniline.}}{\mathbf{N}_3[C(C_6H_4)''_3]^{iv}H_5.} \qquad \underset{\text{Rosaniline.}}{\mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}H_5}$$

The reaction is—

$$\underset{\text{Toluidine.}}{2\mathbf{N}(C_7H_7)H_2} + \underset{\text{Aniline.}}{\mathbf{N}(C_6H_5)H_2} + 3O$$

$$= \underset{\text{Rosaniline.}}{\mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}H_5} + \underset{\text{Water.}}{3\mathbf{O}H_2}.$$

Ordinary rosaniline is obtained from a mixture of aniline and toluidine by the action of various other reagents, such as carbonic chloride, stannic chloride, mercuric chloride, ferric chloride, cupric chloride, the sulphuric and nitric salts of tin and mercury, but arsenic acid is almost exclusively employed for the technical preparation of the salts of this base.

One or more of the five atoms of amidic hydrogen in rosaniline may be replaced by positive radicals, and in this way other bases, the salts of which constitute valuable colouring matters, are produced.

The following are a few of these bases :—

Rosaniline, the base of magenta	$\mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}H_5$.
Phenyl rosaniline, the base of dahline......	$\mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}PhH_4$.
Diphenyl rosaniline, the base of aniline violet.	$\mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}Ph_2H_3$.
Triphenyl rosaniline, the base of aniline blue..	$\mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}Ph_3H_2$.
Tritolyl rosaniline, the base of toluidine blue	$\mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}To_3H_2$.
Triethyl rosaniline, the base of Hofmann's violet	$\mathbf{N}_3[C(C_6H_4)''(C_7H_6)'']^{iv}Et_3H_2$.
Pentamethyl pararosaniline, the base of Paris violet..............	$\mathbf{N}_3[C(C_6H_4)''_3]^{iv}Me_5$.
Chrysaniline, Nicholson's yellow	$\mathbf{N}_3C_{20}H_{17}$.
Paraleukaniline	$\mathbf{N}_3[C(C_6H_4)''H]'''H_6$.

The phenyl derivatives of rosaniline are produced as salts of hydrochloric acid by heating rosaniline hydrochlorate with various proportions of aniline, thus :—

$$\mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}H_5,HCl \quad + \quad \mathbf{N}PhH_2$$

Rosaniline hydrochlorate. Aniline.

$$= \mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}PhH_4,HCl \quad + \quad \mathbf{N}H_3.$$

Phenyl-rosaniline hydrochlorate. Ammonia.

$$\mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}PhH_4,HCl \quad + \quad \mathbf{N}PhH_2$$

Phenyl-rosaniline hydrochlorate. Aniline.

$$= \mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}Ph_2H_3,HCl \quad + \quad \mathbf{N}H_3.$$

Diphenyl-rosaniline hydrochlorate. Ammonia.

$$\mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}Ph_2H_3,HCl \quad + \quad \mathbf{N}PhH_2$$

Diphenyl-rosaniline hydrochlorate. Aniline.

$$= \mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}Ph_3H_2,HCl \quad + \quad \mathbf{N}H_3.$$

Triphenyl-rosaniline hydrochlorate. Ammonia.

The salts of tritolyl rosaniline are formed by analogous reactions, substituting toluidine for aniline.

Triethyl rosaniline is obtained by heating to 100° in close vessel rosaniline with ethylic iodide dissolved alcohol:—

$$\mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}H_5 \quad + \quad 3EtI$$

Rosaniline. Ethylic iodide.

$$= \mathbf{N}_3[C(C_6H_4)''_2(C_7H_6)'']^{iv}Et_3H_2 \quad + \quad 3HI.$$

Trimethyl and triamyl rosaniline are obtained by analogous processes.

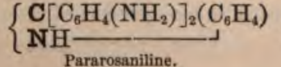
Pentamethylpararosaniline is prepared by the oxidation of dimethylaniline:—

$$3\mathbf{N}(C_6H_5)(CH_3)_2 \ + \ O_3 \ = \ \mathbf{N}_3[C(C_6H_4)''_3]^{iv}(CH_3)_5 = 3\mathbf{O}H_2.$$

Dimethylaniline. Pentamethyl pararosaniline. Water.

Chrysaniline is formed as a secondary product in the manufacture of rosaniline.

Paraleukaniline is obtained by the reduction of pararosaniline in acid solution by means of zinc:—



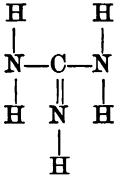
$$\left\{\begin{matrix}\mathbf{C}[C_6H_4(NH_2)]_2(C_6H_4) \\ \mathbf{N}H\underline{\qquad\qquad\quad}\!\lrcorner\end{matrix}\right. \ + \ H_2 \ = \ \mathbf{C}[C_6H_4(NH_2)]_3H.$$

Pararosaniline. Paraleukaniline (triamidotriphenylmethane).

OTHER AMINES.

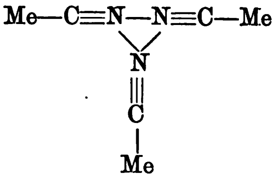
Subjoined are the names and formulæ of a number of organic bases which cannot at present be satisfactorily classified:—

Guanine .... $C_5H_5N_5O$.
Guanidine .... $\mathbf{C}(NH)''(NH_2)(NH_2)$ or $\mathbf{C}(NH)''Ad_2$.

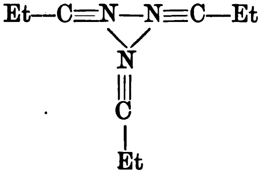


Furfurine .... $C_{15}H_{12}N_2O_3$.
Amarine .... $C_{21}H_{18}N_2$.
Thialdine................ $C_6H_{13}NS_2$.
Dibutyraldine............ $C_8H_{17}NO = \left\{\begin{array}{l}\mathbf{C}\mathrm{PrH}\\ \mathrm{O}\\ \mathbf{C}\mathrm{PrH}\end{array}\right. \mathrm{NH}.$
Acridine .... $C_{12}H_9N$.

Cyanmethine .. $^{vi}(\mathbf{N}_3)^{ix}(CMe)'''_3$ ..



Cyanethine.... $^{vi}(\mathbf{N}_3)^{ix}(CEt)'''_3$ ..



THE NATURAL ALKALOIDS.

Of the constitution of these organic bases very little is known (see, however, p. 232). The following is a list of the chief of them, with the sources whence they are derived :—

Alkaloids from Opium.

Hydrocotarnine	$C_{12}H_{15}NO_3$.
Morphine	$C_{17}H_{19}NO_3$.
Codeine..................	$C_{18}H_{21}NO_3$, OH_2.
Thebaine	$C_{19}H_{21}NO_3$.
Protopine	$C_{20}H_{19}NO_5$.
Papaverine	$C_{20}H_{21}NO_4$.
Cryptopine	$C_{21}H_{23}NO_5$.
Laudanosine..............	$C_{21}H_{27}NO_4$.
Narcotine	$C_{22}H_{23}NO_7$.
Narceine	$C_{23}H_{29}NO_9$.
Gnoscopine	$C_{34}H_{36}N_2O_{11}$.

From Cinchona Bark.

Cinchotine	$C_{19}H_{24}N_2O$.
Quinine..................	$C_{20}H_{24}N_2O_2$.
Cinchonine	$C_{20}H_{24}N_2O$.
Aricine	$C_{23}H_{26}N_2O_4$.

From Nightshade.

Atropine	$C_{17}H_{23}NO_3$.

From Tobacco.

Nicotine..................	$C_{10}H_{14}N_2$.

From Nux vomica.

Strychnine	$C_{21}H_{22}N_2O_2$.
Brucine..................	$C_{23}H_{26}N_2O_4$.

From the Barberry (Berberis vulgaris).

Berberine	$C_{20}H_{17}NO_4$.

From Tea, Coffee, and Cocoa.

Theobromine..............	$C_7H_8N_4O_2$.
Caffeine (*Theine*)	$C_8H_{10}N_4O_2$.

2, 3, 4. *THE PHOSPHINES, ARSINES, STIBINES, AND BISMUTHINES.*

The bases containing phosphorus may be obtained, like the amines, by the displacement of hydrogen in phosphoretted hydrogen. The tertiary compounds only of arsenic, antimony and bismuth are known; and they are produced by reactions of which the following may be regarded as a type:—

$$\underset{\text{Sodic arsenide.}}{\mathbf{As}Na_3} + \underset{\text{Ethylic iodide.}}{3EtI} = \underset{\text{Triethyl arsine.}}{\mathbf{As}Et_3} + \underset{\text{Sodic iodide.}}{3NaI.}$$

Primary and secondary phosphines are obtained by the action of methylic or ethylic iodide and zincic oxide upon phosphonic iodide. With ethylic iodide the following reactions occur:—

$$\underset{\text{Phosphonic iodide.}}{2\mathbf{P}H_4I} + \underset{\text{Ethylic iodide.}}{2EtI} + \mathbf{Zn}O = \underset{\text{Ethyl-phosphonic iodide.}}{2\mathbf{P}EtH_3I} + \mathbf{Zn}I_2 + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

$$\underset{\text{Phosphonic iodide.}}{2\mathbf{P}H_4I} + \underset{\text{Ethylic iodide.}}{4EtI} + 3\mathbf{Zn}O = \underset{\text{Diethyl-phosphonic zincic iodide.}}{2\mathbf{P}Et_2H(ZnI)I} + \underset{\text{Water.}}{3\mathbf{O}H_2} + \mathbf{Zn}I_2.$$

These reactions take place side by side; but the primary and secondary phosphines are readily separated from each other by the consecutive action of water and alkalies upon the products of the above operation.

The addition of water to the mixed product liberates the primary phosphine from its compound, whilst the compound of the secondary phosphine resists even boiling water, but easily decomposes under the influence of alkalies.

The tertiary phosphines are produced by the action of the zinc compounds of the monad positive radicals upon phosphorous chloride:—

$$\underset{\text{Zincic ethide.}}{3\mathbf{Zn}\mathrm{Et}_2} + \underset{\text{Phosphorous chloride.}}{2\mathbf{P}\mathrm{Cl}_3} = \underset{\text{Triethyl phosphine.}}{2\mathbf{P}\mathrm{Et}_3} + \underset{\text{Zincic chloride.}}{3\mathbf{Zn}\mathrm{Cl}_2}.$$

They may also be obtained in combination with hydriodic acid by the action of phosphonic iodide upon the alcohols:—

$$\underset{\text{Phosphonic iodide.}}{\mathbf{P}\mathrm{H}_4\mathrm{I}} + \underset{\text{Ethylic alcohol.}}{3\mathrm{EtHo}} = \underset{\text{Triethyl-phosphonic iodide.}}{\mathbf{P}\mathrm{Et}_3\mathrm{HI}} + \underset{\text{Water.}}{3\mathbf{O}\mathrm{H}_2}.$$

By the action of alkalies upon triethyl-phosphonic iodide triethyl phosphine is liberated:—

$$\underset{\text{Triethyl-phosphonic iodide.}}{\mathbf{P}\mathrm{Et}_3\mathrm{HI}} + \mathrm{KHo} = \underset{\text{Triethyl-phosphine.}}{\mathbf{P}\mathrm{Et}_3} + \mathrm{KI} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2}.$$

The following Table contains the names of the known phosphines, arsines, and stibines:—

Primary Phosphines.

	Formula.	Boiling-point.
Methyl phosphine	$\mathbf{P}\mathrm{MeH}_2$......	−14°
Ethyl phosphine........	$\mathbf{P}\mathrm{EtH}_2$......	25

Secondary Phosphines.

Dimethyl phosphine	$\mathbf{P}\mathrm{Me}_2\mathrm{H}$......	25
Diethyl phosphine	$\mathbf{P}\mathrm{Et}_2\mathrm{H}$......	85

Tertiary Phosphines.

Trimethyl phosphine	$\mathbf{P}\mathrm{Me}_3$	41
Triethyl phosphine......	$\mathbf{P}\mathrm{Et}_3$........	127·5

Tertiary Arsines.

Trimethyl arsine........	$\mathbf{As}\mathrm{Me}_3$	120
Triethyl arsine..........	$\mathbf{As}\mathrm{Et}_3$	140

Tertiary Stibines.

	Formula.	Boiling-point.
Trimethyl stibine	$SbMe_3$	—
Triethyl stibine	$SbEt_3$	158°
Triamyl stibine	$SbAy_3$	—

Tertiary Bismuthine.

Triethyl bismuthine	$BiEt_3$	—

Character.—The phosphines, arsines, stibines, and bismuthines possess very energetic affinities for negative elements. Many of them are spontaneously inflammable in air and oxygen. Most, probably all, unite with an atom of oxygen or a molecule of chlorine, bromine, or iodine, forming compounds in which the grouping element becomes pentadic. Thus, by the absorption of oxygen, triethyl-phosphine is transformed into phosphoric triethoxide:—

$$\underset{\text{Triethyl-phosphine.}}{PEt_3} + O = \underset{\text{Phosphoric triethoxide.}}{PEt_3O}.$$

5. *OXYBASES.*

These compounds are only known in the arsenic series.

Arsenious oxybases.

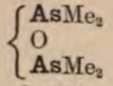
Only one of these, cacodylic oxide, has been carefully investigated.

By the distillation of potassic acetate with arsenious anhydride, a compound known as cacodyl, $'As''_2Me_4$, is produced. This substance may also be prepared by the action of methylic iodide upon an alloy of sodium and arsenic containing $'As''_2Na_4$:—

$$\underset{\text{Sodic arsenide.}}{'As''_2Na_4} + \underset{\text{Methylic iodide.}}{4MeI} = \underset{\text{Cacodyl.}}{'As''_2Me_4} + \underset{\text{Sodic iodide.}}{4NaI}.$$

By allowing cacodyl to absorb oxygen slowly, an oily liquid containing cacodylic oxide (As_2Me_4O) is formed.

This oxybase does not appear to unite with oxygen acids, but it is attacked by hydrochloric acid, forming cacodylic chloride:—



$$\underset{\text{Cacodylic oxide.}}{\left\{\begin{matrix}\mathbf{As}Me_2\\ O\\ \mathbf{As}Me_2\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Cacodylic chloride.}}{2\mathbf{As}Me_2Cl} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

Cacodylic oxide, when exposed to moist air, absorbs water and oxygen, forming cacodylic acid:—

$$\underset{\text{Cacodylic oxide.}}{\mathbf{As}_2Me_4O} + O_2 + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Cacodylic acid.}}{2\mathbf{As}Me_2OHo}.$$

CHAPTER XXIX.

ORGANIC COMPOUNDS OF TRIAD NITROGEN AND OF ITS ANALOGUES (*continued*).

NEUTRAL SECTION.

1. *THE AMIDES.*

These compounds are formed by the substitution of amidogen (NH_2) for the oxatylic hydroxyl of organic acids. They are most conveniently written on the diadelphic type, but may also be formulated upon the ammonia type.

If the acid contain only one semimolecule of oxatyl, a monamide is the result; if two semimolecules of oxatyl are present in the acid, a diamide is generally formed, &c. Secondary and tertiary compounds can also be produced, as in the case of the amines; but they belong to the negative section of this family.

A. *MONAMIDES.*

I. *Primary Monamides.*

Acetamide:—

$$\left\{\begin{array}{l}\mathrm{CMeO}\\ \mathrm{NH_2}\end{array}\right. \text{ or } \mathrm{NH_2(CMeO)}, \text{ or } \left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COAd}\end{array}\right. .$$

Chloracetamide:—

$$\left\{\begin{array}{l}\mathrm{C(CH_2Cl)O}\\ \mathrm{NH_2}\end{array}\right. \text{ or } \mathrm{NH_2[C(CH_2Cl)O]}, \text{ or } \left\{\begin{array}{l}\mathrm{CH_2Cl}\\ \mathrm{COAd}\end{array}\right. .$$

Benzamide:—

$$\left\{\begin{array}{l}\mathrm{C(C_6H_5)O}\\ \mathrm{NH_2}\end{array}\right. \text{ or } \mathrm{NH_2[C(C_6H_5)O]}, \text{ or } \left\{\begin{array}{l}\mathrm{C_6H_5}\\ \mathrm{COAd}\end{array}\right. .$$

Formation.—1. By the distillation of the ammonic salts of the monobasic acids:—

$$\underset{\text{Ammonic acetate.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO(N^vH_4O)}\end{array}\right.} = \underset{\text{Acetamide.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO(N'''H_2)}\end{array}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

2. By the action of ammonia upon the chloracids:—

$$\underset{\text{Acetylic chloride.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COCl}\end{array}\right.} + \underset{\text{Ammonia.}}{\mathrm{NH_3}} = \underset{\text{Acetamide.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO(N'''H_2)}\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}}.$$

3. By the action of ammonia on the ethereal salts of the monobasic acids:—

$$\underset{\text{Ethylic acetate.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COEto}\end{array}\right.} + \underset{\text{Ammonia.}}{\mathrm{NH_3}} = \underset{\text{Acetamide.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO(N'''H_2)}\end{array}\right.} + \underset{\text{Alcohol.}}{\mathrm{EtHo}}.$$

Reactions.—1. Boiled with aqueous solutions of acids, the primary monamides yield ammonic salts and acids:—

$$\underset{\text{Acetamide.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO(N'''H_2)}\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}} + \underset{\text{Water.}}{\mathrm{OH_2}} = \underset{\text{Ammonic chloride.}}{\mathrm{NH_4Cl}} + \underset{\text{Acetic acid.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COHo}\end{array}\right.} .$$

2. Boiled with potassic hydrate, ammonia is evolved, and a potassic salt, corresponding to the amide, is formed.

$$\underset{\text{Acetamide.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO(N'''H_2)}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{\mathrm{KHo}} = \underset{\text{Ammonia.}}{\mathbf{N}\mathrm{H_3}} + \underset{\text{Potassic acetate.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COKo}\end{array}\right.}$$

II. *Secondary Monamides.*

Diacetimide.... $\mathbf{N}(\mathrm{CMeO})_2\mathrm{H}$ or $\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO}\\ \mathrm{NH}.\\ \mathrm{CO}\\ \mathrm{CH_3}\end{array}\right.$

Succinimide.... $\mathbf{N}\mathrm{H}\left[\left\{\begin{array}{l}\mathrm{CO}\\ \mathrm{C_2H_4}\\ \mathrm{CO}\end{array}\right.\right]''$ or $\left\{\begin{array}{l}\mathrm{CO}\urcorner\\ \mathrm{Et''}(\mathrm{N'''H})''.\\ \mathrm{CO}\lrcorner\end{array}\right.$

These bodies possess a negative character, and are treated of under the negative section of this class as *imides of negative radicals* (p. 251).

Tertiary monamides are little known. They are the *nitrides of negative radicals* (see p. 251).

B. *DIAMIDES.*

The diamides may be regarded as derived from two molecules of ammonia, by the substitution of a dyad negative radical for two atoms of hydrogen; or they may be considered to be formed by the substitution of amidogen for the hydroxyl contained in the two semimolecules of oxatyl in dibasic acids:—

Primary Diamides.

Oxamide .. $\left\{\begin{array}{l}\mathbf{N}\mathrm{H_2}\\ (\mathrm{C_2O_2})''\\ \mathbf{N}\mathrm{H_2}\end{array}\right.$ or $\left\{\begin{array}{l}\mathrm{COAd}\\ \mathrm{COAd}\end{array}\right.$

Succinamide.. $\mathbf{N}_2\mathrm{H_4}(\mathrm{C_4H_4O_2})''$ or $\mathbf{N}_2\mathrm{H_4}\left[\left\{\begin{array}{l}\mathrm{CO}\\ \mathrm{Et''}\\ \mathrm{CO}\end{array}\right.\right]''$, or $\left\{\begin{array}{l}\mathrm{COAd}\\ \mathrm{Et''}\\ \mathrm{COAd}\end{array}\right.$.

Formation.—1. By the action of heat upon the normal ammonic salts of dibasic acids:—

$$\underset{\text{Ammonic oxalate.}}{\left\{\begin{matrix}\mathrm{CO(N^{v}H_4O)}\\ \mathrm{CO(N^{v}H_4O)}\end{matrix}\right.} = \underset{\text{Oxamide.}}{\left\{\begin{matrix}\mathrm{CO(N'''H_2)}\\ \mathrm{CO(N'''H_2)}\end{matrix}\right.} + \underset{\text{Water.}}{\mathrm{2OH_2}}.$$

2. By the action of ammonia on the ethereal salts of dibasic acids:—

$$\underset{\text{Ethylic oxalate.}}{\left\{\begin{matrix}\mathrm{COEto}\\ \mathrm{COEto}\end{matrix}\right.} + \underset{\text{Ammonia.}}{\mathrm{2NH_3}} = \underset{\text{Oxamide.}}{\left\{\begin{matrix}\mathrm{CO(N'''H_2)}\\ \mathrm{CO(N'''H_2)}\end{matrix}\right.} + \underset{\text{Alcohol.}}{\mathrm{2EtHo}}.$$

3. By the action of ammonia on the chloro-dibasic acids:—

$$\underset{\text{Ammonia.}}{\mathrm{4NH_3}} + \underset{\text{Succinylic chloride.}}{\left\{\begin{matrix}\mathrm{COCl}\\ \mathrm{Et''}\\ \mathrm{COCl}\end{matrix}\right.} = \underset{\text{Succinamide.}}{\left\{\begin{matrix}\mathrm{CO(N'''H_2)}\\ \mathrm{Et''}\\ \mathrm{CO(N'''H_2)}\end{matrix}\right.} + \underset{\text{Ammonic chloride.}}{\mathrm{2NH_4Cl}}.$$

The *secondary* and *tertiary diamides* are but little known.

C. *TRIAMIDES.*

Primary Triamides.—The primary triamides may be regarded as derived from tribasic acids by the substitution of amidogen for the hydroxyl contained in the three semimolecules of oxatyl of these acids, or as derived from three molecules of ammonia by the replacement of three atoms of hydrogen by the residue of a tribasic acid. A good example of a triamide is

$$\text{Citramide} \ldots\ldots \left\{\begin{matrix}\mathrm{CH_2(COAd)}\\ \mathrm{CHo(COAd)}\\ \mathrm{CH_2(COAd)}\end{matrix}\right. \text{ or } \mathrm{N_3H_6(C_6H_5O_4)'''}.$$

Citramide is formed by the action of ammonia on ethylic citrate.

Secondary and *tertiary triamides* have not yet been formed.

2. *THE ALKALAMIDES.*

These compounds occupy an intermediate position between the amines and the amides. They are derived from ammonia by the substitution of part of the hydrogen by positive, and part by negative radicals; and inasmuch as two atoms at least of hydrogen must be so substituted, no primary alkalamide can exist.

Secondary and tertiary monalkalamides, dialkalamides, and trialkalamides are known.

Ethyl acetamide	$\mathbf{N}HEt(CMeO)$.
Ethyl diacetamide	$\mathbf{N}Et(CMeO)_2$.
Diethyl oxamide	$\mathbf{N}_2H_2Et_2(C_2O_2)''$.
Diphenyl-carbonyl-oxalyl diamide	$\mathbf{N}_2(C_6H_5)_2(CO)''(C_2O_2)''$.
Citryl-triphenyl-triamide	$\mathbf{N}_3H_3(C_6H_5)_3(C_6H_5O_4)'''$.

The alkalamides incline towards a positive character, their degree of alkalinity being about equal to that of urea.

3. *THE TRICHLORINATED AND TRIBROMINATED AMINES.*

If the hydrogen in an amine be gradually substituted by chlorine or bromine, the basic character of the amine gradually diminishes, and finally a neutral compound is obtained.

This reaction has been studied in the case of aniline, which loses basic energy by the successive replacement of two atoms of hydrogen, and finally becomes neutral by the substitution of three atoms of chlorine or bromine for three of hydrogen:—

$\mathbf{N}H_2(C_6H_5)$.	$\mathbf{N}H_2(C_6H_4Cl)$.	$\mathbf{N}H_2(C_6H_3Cl_2)$.	$\mathbf{N}H_2(C_6H_2Cl_3)$.
Aniline.	Chloraniline.	Dichloraniline.	Trichloraniline.

4. *THE HALOID COMPOUNDS OF OXYBASES.*

These bodies are only known in the arsenic series; they are formed by the action of chlorine, bromine, or iodine upon cacodyl and its homologues, or of hydrochloric acid, hydrobromic acid, or hydriodic acid upon the oxybases.

General formula .... $\mathbf{As}(C_nH_{2n+1})_2Cl$.

NEGATIVE SECTION.

THE IMIDES AND NITRIDES.

$$\text{General formula..}\begin{cases}\text{of imides..} & NH(C_nH_{2n-1}O)_2,\\ \text{of nitrides.} & N(C_nH_{2n-1}O)_3.\end{cases}$$

Formation.—By the action of chloracids (the so-called chlorides of negative radicals) upon amides:—

$$\underset{\text{Acetamide.}}{NH_2(CMeO)} + \underset{\text{Acetylic chloride.}}{CMeOCl} = \underset{\text{Diacetimide.}}{NH(CMeO)_2} + \underset{\text{Hydrochloric acid.}}{HCl.}$$

A repetition of this reaction gives acetylic nitride, which may also be obtained by heating a mixture of acetonitrile and acetic anhydride to 200°.

An imide may also be formed by the substitution of a dyad negative radical for two atoms of hydrogen in ammonia, thus:—

$$\text{Succinimide......}\ NH(C_4H_4O_2)'',\ \text{or}\ NH\left[\left\{\begin{matrix}CO\\ Et''\\ CO\end{matrix}\right.\right]''.$$

These bodies have hitherto received but little attention.

CHAPTER XXX.

II. *COMPOUNDS OF PENTAD NITROGEN AND OF ITS ANALOGUES.*

This class of compounds contains the following series:—

Positive.	*Neutral.*	*Negative.*
1. Caustic Nitrogen bases	1. Salts of Amines.	1. Organic arsenic acids, oxychlorides, and chlorides.
2. „ Phosphorus bases.	2. „ Phosphines.	2. Organic antimonic acids.
3. „ Arsenic bases.	3. „ Arsines.	3. Organic phosphoric acids.
4. „ Antimony bases.	4. „ Stibines.	
5. Oxyarsenic bases.	5. „ Oxyarsenic bases.	
6. Oxyantimonic bases.	6. „ Oxantimonic bases.	

POSITIVE COMPOUNDS.

1. *Caustic Nitrogen Bases.*—

General formula. . . . $\mathbf{N}(C_nH_{2n+1})_4Ho$.

In each positive radicle n must be a positive integer. The radicals need not be all of the same atomic weight.

Formation.—By the action of argentic hydrate upon the iodides of the compound ammoniums:—

$$\underset{\text{Tetrethylammonic iodide.}}{\mathbf{N}Et_4I} + \underset{\text{Argentic hydrate.}}{AgHo} = \underset{\text{Tetrethylammonic hydrate.}}{\mathbf{N}Et_4Ho} + \underset{\text{Argentic iodide.}}{AgI.}$$

2. *Caustic Phosphorus Bases.*

3. *Caustic Arsenic Bases.*

4. *Caustic Antimony Bases.*

By displacing the **N** in the above general formula and in the equation by **P**, **As**, and **Sb**, the constitution and formation of these three series of compounds will be expressed.

5. *Oxyarsenic Bases.*—These bodies, which are diacid bases, are obtained by the slow oxidation of the tertiary monarsines:—

$$\underset{\text{Tertiary monarsine.}}{\mathbf{As}(C_nH_{2n+1})_3} + O = \underset{\text{Oxyarsenic base.}}{\mathbf{As}(C_nH_{2n+1})_3O.}$$

6. *Oxyantimonic Bases.*—These are formed in a manner exactly analogous to that in which the oxyarsenic bases are produced.

NEUTRAL COMPOUNDS.

1. *Salts of Amines.*

General formulæ:—

$$\mathbf{N}(C_nH_{2n+1})(C_mH_{2m+1})_3Cl.$$
$$\mathbf{N}_2(C_nH_{2n})''(C_mH_{2m})''_2H_2Cl_2.$$
$$\mathbf{N}_3(C_nH_{2n-1})'''(C_mH_{2m-1})'''_2H_3Cl_3.$$

In the first formula m may $=0$; in the second, C_mH_{2m} may be displaced by H_2; and in the third, C_mH_{2m-1} may be substituted by H_3.

Formation.—Like the analogous compounds of ammonia, the salts of the amines are formed by the direct union of acids with the amines without elimination of water, thus:—

$$\underset{\text{Ethylamine.}}{NEtH_2} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ethylammonic chloride.}}{NEtH_3Cl.}$$

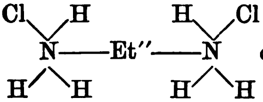
The haloid salts of the amines may also be produced by the union of the haloid ethers of the monad positive radicals with the amines (for reaction see p. 227).

Character.—The salts of the diamines and triamines are often found to contain only one molecule of acid, instead of two or three as shown in the above general formulæ, which indicate the composition of the normal salts. The nitrogen atoms are in such cases united together by one of the bonds of each, besides being linked by the polyad radicals, thus:—

$$'N^{iv}{}_2(C_nH_{2n})''(C_mH_{2m})''{}_2H(NO_3);$$
$${}^{iv}(N_3)^{xi}(C_nH_{2n-1})'''(C_mH_{2m-1})'''{}_2HCl.$$

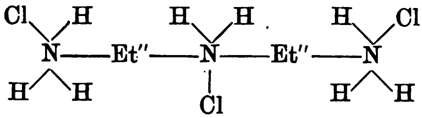
The difference between these two classes of salts will be rendered more evident by a comparison of the following graphic and symbolic formulæ:—

Normal Salts.



$$\text{or } N_2H_6Et''Cl_2, \text{ or} \begin{cases} NH_3Cl \\ Et'' \\ NH_3Cl \end{cases}.$$

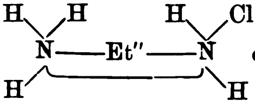
Ethylene-diammonic dichloride.



Diethylene-triammonic trichloride.

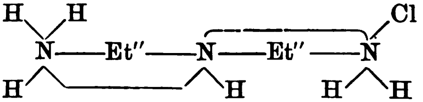
$$\text{or } N_3H_8Et''{}_2Cl_3 \text{ or} \begin{cases} NH_3Cl \\ Et'' \\ NH_2Cl. \\ Et'' \\ NH_3Cl \end{cases}$$

Monacid Salts.



or $'N^{iv}_2H_5Et''Cl$ or $\left\{\begin{matrix}NH_3\\NH_2\end{matrix}\right.ClEt''$.

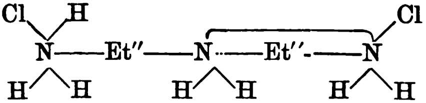
Ethylene-diammonic monochloride.



Diethylene-triammonic monochloride.

$$\text{or } ^{iv}(N_3)^{xi}H_6Et''_2Cl \text{ or } \left\{\begin{array}{ll}NH_3 & \\ & Et'' \\ NH & \\ & Et'' \\ NH_2Cl & \end{array}\right.$$

Diacid Salt.



Diethylene-triammonic dichloride.

$$\text{or } ''(N_3)^{xiii}H_7Et''_2Cl_2 \text{ or } \left\{\begin{array}{ll}NH_3Cl & \\ & Et'' \\ NH_2 & \\ & Et''. \\ NH_2Cl & \end{array}\right.$$

2. *Salts of Phosphines.*
3. *Salts of Arsines.*
4. *Salts of Stibines.*

These three series of salts all present close analogies with the salts of the amines both in constitution and in the mode of their formation. The mode of formation of several of them is shown at pages 243 and 244.

5. *Salts of Oxyarsenic Bases.*

$$As(C_nH_{2n+1})_3Cl_2.$$

Formation.—By the action of acids on the oxyarsenic bases:—

$$\underset{\text{Arsenic trimethoxide.}}{\mathbf{As}Me_3O} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Arsenic trimetho-dichloride.}}{\mathbf{As}Me_3Cl_2} + \underset{\text{Water.}}{\mathbf{O}H_2}$$

6. *Salts of Oxyantimonic Bases.*

These resemble the previous salts in formation and constitution.

NEGATIVE COMPOUNDS.

1. *Organic Arsenic Acids, Oxychlorides, and Chlorides.*

The following are the principal bodies of this class:—

Monomethylarsenic acid........	$\mathbf{As}MeOHo_2$.
Arsenic oxydichlormethide......	$\mathbf{As}MeOCl_2$.
Arsenic tetrachlormethide......	$\mathbf{As}MeCl_4$.
Cacodylic acid................	$\mathbf{As}Me_2OHo$.
Cacodylic trichloride	$\mathbf{As}Me_2Cl_3$.

2. *Organic Antimonic Acids.*

No exploration of this series has yet been made. The members of it will doubtless be found to have close analogies with the corresponding series of arsenic compounds.

3. *Organic Phosphoric Acids.*

Monomethylphosphoric acid, $\mathbf{P}MeOHo_2$, and dimethylphosphoric acid, $\mathbf{P}Me_2OHo$, have been prepared.

CHAPTER XXXI.

ORGANO-BORON AND SILICON COMPOUNDS.

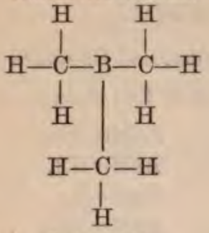
This family is divided into the two following classes:—

1. Organo-boron compounds.
2. Organo-silicon compounds.

1. *Organo-boron compounds.*

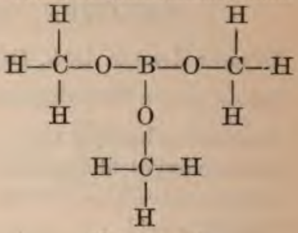
These compounds contain boron directly united with the carbon of monad positive radicals, and are thus distinguished from organic compounds containing boron, as seen in the following formulæ :—

Organo-boron compound.



Boric methide.

Organic compound containing boron.



Methylic borate.

The organo-boron compounds are produced by the replacement of methoxyl or ethoxyl in methylic or ethylic borate by monad positive radicals. Hitherto only the radicals methyl and ethyl have been thus combined with boron.

BORIC METHIDE.

$\mathbf{B}(CH_3)_3$, or $\mathbf{B}Me_3$.

Molecular weight = 56. *Molecular volume* ☐☐. 1 *litre of boric methide gas weighs* 28 *criths. Condenses at* 10° *under a pressure of four atmospheres.*

Preparation.—By adding to ethylic borate an ethereal solution of zincic methide, when boric methide is evolved as gas :—

$$\underset{\text{Ethylic borate.}}{2\mathbf{B}Eto_3} + \underset{\text{Zincic methide.}}{3\mathbf{Zn}Me_2} = \underset{\text{Boric methide.}}{2\mathbf{B}Me_3} + \underset{\text{Zincic ethylate.}}{3\mathbf{Zn}Eto_2}.$$

Reactions.—1. Inflames spontaneously in air or oxygen.

2. Combines energetically with ammonia, forming ammonia-boric methide :—

$$\underset{\text{Ammonia.}}{\mathbf{NH_3}} + \underset{\text{Boric methide.}}{\mathbf{BMe_3}} = \underset{\text{Ammonia-boric methide.}}{\mathbf{NH_3,BMe_3}}.$$

3. Boric methide combines readily with potash, soda, lime, and baryta, forming compounds the composition of which is not known with certainty.

AMMONIA-BORIC METHIDE.

$\mathbf{NH_3,BMe_3}$.

Molecular weight = 73. *Molecular volume* (*anomalous*) ⊞. *Fuses at* 56°. *Boils at* 110°. 1 *litre of ammonia-boric methide vapour weighs* 18·25 *criths.*

Formed as above described.

Reactions.—1. Cupric chloride absorbs ammonia from the vapour of ammonia-boric methide, reducing the volume of the vapour to one half and leaving boric methide gas:—

$$\underset{\text{Ammonia-boric methide.}}{6(\mathbf{NH_3,BMe_3})} + 2\mathbf{CuCl_2} = \underset{\text{Ammonia-cupric chloride.}}{2\mathbf{CuCl_2,6NH_3}} + \underset{\text{Boric methide.}}{6\mathbf{BMe_3}}.$$

2. Ammonia-boric methide is readily decomposed by acids; even carbonic acid decomposes it. With hydrochloric acid the reaction is:—

$$\underset{\text{Ammonia-boric methide.}}{\mathbf{NH_3,BMe_3}} + HCl = \underset{\text{Ammonic chloride.}}{\mathbf{NH_4Cl}} + \underset{\text{Boric methide.}}{\mathbf{BMe_3}}.$$

BORIC ETHIDE.

$\mathbf{B}(C_2H_5)_3$ or $\mathbf{BEt_3}$.

Molecular weight = 98. *Molecular volume* □□. 1 *litre of boric ethide vapour weighs* 49 *criths. Boils at* 95° C. *Sp. gr. of liquid* 0·6961 at 23°.

Preparation.—1. By the action of zincic ethide upon ethylic borate:—

$$\underset{\text{Ethylic borate.}}{2BEto_3} + \underset{\text{Zincic ethide.}}{3ZnEt_2} = \underset{\text{Boric ethide.}}{2BEt_3} + \underset{\text{Zincic ethylate.}}{3ZnEto_2.}$$

2. By the action of zincic ethide upon boric chloride:—

$$\underset{\text{Boric chloride.}}{BCl_3} + \underset{\text{Zincic ethide.}}{3ZnEt_2} = \underset{\text{Boric ethide.}}{BEt_3} + \underset{\text{Zincic ethochloride.}}{3ZnEtCl.}$$

Reactions.—1. Inflames spontaneously in air, and explodes in oxygen.

2. Allowed to oxidize gradually, boric ethide forms boric etho-diethylate:—

$$BEt_3 + O_2 = BEtEto_2.$$

3. Heated with hydrochloric acid to 99°, it slowly evolves ethylic hydride, and is converted into boric dietho-chloride:—

$$\underset{\text{Boric ethide.}}{BEt_3} + HCl = \underset{\text{Boric dietho-chloride.}}{BEt_2Cl} + \underset{\text{Ethylic hydride.}}{EtH.}$$

4. Boric ethide combines very energetically with ammoniacal gas, forming ammonia-boric ethide:—

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Boric ethide.}}{BEt_3} = \underset{\text{Ammonia-boric ethide.}}{NH_3,BEt_3.}$$

BORIC DIETHETHYLATE.

Boils at 102—103°.

Preparation.—By the action of zincic ethide upon boric ethylate, in the proportion of two molecules of the former to one of the latter:—

$$\underset{\text{Boric ethylate.}}{BEto_3} + \underset{\text{Zincic ethide.}}{2ZnEt_2} = \underset{\text{Boric diethethylate.}}{BEt_2Eto} + \underset{\text{Zincic ethethylate.}}{2ZnEtEto.}$$

Reaction.—Water decomposes it, yielding *boric diethohydrate:*—

$$\underset{\text{Boric diethethylate.}}{BEt_2Eto} + \underset{\text{Water.}}{OH_2} = \underset{\text{Boric diethohydrate.}}{BEt_2Ho} + \underset{\text{Alcohol.}}{EtHo.}$$

BORIC ETHO-DIETHYLATE.

$BEtEto_2$.

Boils at 125° C.

Preparation.—By the slow action of oxygen upon boric ethide as above described.

Reaction.—In contact with water it is instantly decomposed, forming *boric etho-dihydrate*:—

$$\underset{\text{Boric etho-diethylate.}}{BEtEto_2} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Boric etho-dihydrate.}}{BEtHo_2} + \underset{\text{Alcohol.}}{2HEto.}$$

DIBORIC ETHOPENTETHYLATE.

$BEtEto_2,BEto_3$.

Boils at 120°. *Molecular volume* (*anomalous*) ⊞.

Preparation.—By the mutual action of zincic ethide and boric ethylate in the proportion of one molecule of the former to two of the latter:—

$$\underset{\text{Boric ethylate.}}{2BEto_3} + \underset{\text{Zincic ethide.}}{ZnEt_2} = \underset{\text{Diboric ethopentethylate.}}{BEtEto_2,BEto_3} + \underset{\text{Zincic ethethylate.}}{ZnEtEto.}$$

Reaction.—With water it forms boric acid and boric etho-dihydrate:—

$$\underset{\text{Diboric ethopentethylate.}}{BEtEto_2,BEto_3} + \underset{\text{Water.}}{5OH_2} = \underset{\text{Boric ethodihydrate.}}{BEtHo_2} + \underset{\text{Boric acid.}}{BHo_3} + \underset{\text{Alcohol.}}{5EtHo.}$$

AMMONIA-BORIC ETHIDE.

NH_3,BEt_3.

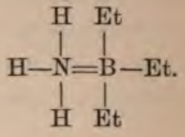
Formed by the union of ammonia gas with boric ethide as above described.

Reaction.—Decomposed by acids but not by carbonic acid. With hydrochloric acid the reaction is as follows:—

$$\underset{\text{Ammonia-boric ethide.}}{NH_3,BEt_3} + HCl = \underset{\text{Ammonic chloride.}}{NH_4Cl} + \underset{\text{Boric ethide.}}{BEt_3.}$$

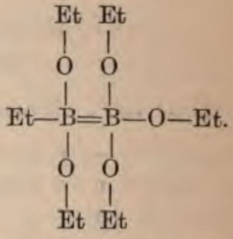
The existence of such compounds as ammonia-boric ethide and diboric ethopenthylate first pointed to the possibility of a pentadic condition of the boron atom corresponding to that of nitrogen, phosphorus, and arsenic. On this supposition the compounds just named would have the following constitutional formulæ :—

Ammonia-boric ethide ..



$$\mathrm{H{-}\overset{H}{\underset{H}{N}}{=}\overset{Et}{\underset{Et}{B}}{-}Et.}$$

Diboric ethopentethylate ..



$$\mathrm{Et{-}\overset{\overset{Et}{O}}{\underset{\underset{Et}{O}}{B}}{=}\overset{\overset{Et}{O}}{\underset{\underset{Et}{O}}{B}}{-}O{-}Et.}$$

Still more definite proof of this pentadic character has lately been obtained by the preparation of perboric phenotetrachloride (**B**$PhCl_4$). This compound is stable only in a freezing mixture and decomposes spontaneously at ordinary temperatures into boric phenodichloride (**B**$PhCl_2$) and chlorine.

2. *Organo-silicon compounds.*

The great similarity in chemical functions between carbon and silicon seems to justify the anticipation that a great number of compounds of silicon will be produced analogous in constitution to the organic compounds. Already several such compounds are known, as for instance :—

Silico-compounds.	Organic analogues.
SiH_4. Silicic hydride.	**CH_4.** Marsh gas.
$SiHCl_3$. Silicon chloroform.	**$CHCl_3$.** Chloroform.

$$\left\{\begin{array}{l}\mathbf{Si}\mathrm{HO}\\ \mathrm{O}\\ \mathbf{Si}\mathrm{HO}\end{array}\right. .$$

Silicoformic anhydride.

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{HO}\\ \mathrm{O}\\ \mathbf{C}\mathrm{HO}\end{array}\right. .$$

Unknown formic anhydride.

Following the analogy of organic compounds, the substitution of one of the atoms of hydrogen in silicic hydride by the hitherto unknown radical silicon methyl ($\mathbf{Si}H_3$) would yield a body constituted like the molecule of methyl or ethylic hydride,

$$\left\{\begin{array}{l}\mathbf{Si}H_3\\ \mathbf{Si}H_3\end{array}\right. .$$

From this, silicoethylic chloride ($\mathbf{Si}_2H_5Cl$) ought to be obtained; and then, by the substitution of hydroxyl for chlorine, the silicon-analogue of common alcohol ($\mathbf{Si}_2H_5Ho$). None of these compounds containing silicon directly combined with silicon have hitherto been formed; indeed, unlike the tetrad elements, carbon, tin, and titanium, silicon appears to have little tendency to form such compounds. Amongst the host of silicon minerals there is not one in which the assumption of the existence of silicon combined directly with silicon is admissible. Disilicic hexachloride ($\mathbf{Si}_2Cl_6$) has, however, been recently formed.

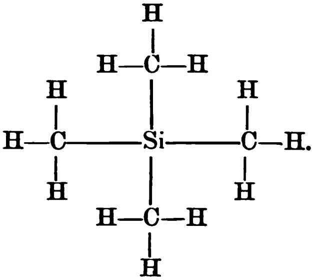
But, although these true silicon analogues of the more complex organic compounds have not hitherto been obtained, yet a large number of bodies which contain silicon atoms directly combined with carbon have been synthetically produced; and many of these substances exhibit interesting analogies with corresponding compounds containing carbon in the place of silicon. These are the bodies which are included in the class of *organo-silicon compounds*. The following Table contains the names and constitutional formulæ of the chief members of this class, together with those of their derivatives, such as ethylic silicate ($\mathbf{Si}Eto_4$), which do not, strictly speaking, belong to it, inasmuch as they no longer contain silicon directly combined with carbon:—

Name.	Formula.	Boiling-point.
Silicic methide	$SiMe_4$	30·5°
Disilicic oxy-hexamethylate	$\left\{\begin{array}{l}SiMeo_3\\O\\SiMeo_3\end{array}\right.$	202
Silicic methylate	$SiMeo_4$	121
Silicic ethide	$SiEt_4$	152·5
Silicic dimethylate ethylate	$SiMeo_2Eto_2$	145
Silicic chlortriethylate	$SiClEto_3$	156
Silicic dichlorethylate	$SiCl_2Eto_2$	—
Silicic ethylate	$SiEto_4$	166·5
Silicic triethylate amylate	$SiEto_3Ayo$	220
Disilicic oxy-hexaethylate	$\left\{\begin{array}{l}SiEto_3\\O\\SiEto_3\end{array}\right.$	235
Disilicic oxy-hexaethide	$\left\{\begin{array}{l}SiEt_3\\O\\SiEt_3\end{array}\right.$	227
Silicic hydrotriethylate	$SiHEto_3$	134
Silicic ethotriethylate	$SiEtEto_3$	158·5
Silicic dieth-ethylate	$SiEt_2Eto_2$	155·5
Silicic trieth-ethylate	$SiEt_3Eto$	153
Silicic dietho-chlorethylate	$SiEt_2ClEto$	148
Silicic chlortriethide	$SiEt_3Cl$	143·5
Silicic dichlorethide	$SiEt_2Cl_2$	129
Silicic trichlorethide	$SiEtCl_3$	—
Silicic diethoxide	$SiEt_2O$	—
Siliconony lic chloride	$\left\{\begin{array}{l}SiEt_3\\CMeHCl\end{array}\right.$	185
Siliconony lic alcohol	$\left\{\begin{array}{l}SiEt_3\\CMeHHo\end{array}\right.$	190
Siliconony lic acetate	$\left\{\begin{array}{l}CH_3\\CO(SiC_8H_{19}O)\end{array}\right.$	211
Silicic aceto-triethylate	$\left\{\begin{array}{l}SiEto_3\\O\\COMe\end{array}\right.$	—
Silicic acetylate	$Si(COMe)_4$	—

Name.	Formula.	Boiling-point.
Silicopropionic acid	$\begin{cases} \mathrm{CMeH_2} \\ \mathrm{SiOHo} \end{cases}$	—
Silicic triethohydrate (*Triethyl-silicol*)	$SiEt_3Ho$	153·5°

SILICIC METHIDE.

$Si(CH_3)_4$
or
$SiMe_4$.



Molecular weight = 88·5. *Molecular volume* ☐☐. 1 *litre of silicic methide vapour weighs* 44·25 *criths. Boils at* 30°·5.

Formation.—By the action of zincic methide upon silicic chloride at a temperature of from 120° to 200°.

$SiCl_4$	+	$2ZnMe_2$	=	$SiMe_4$	+	$2ZnCl_2$.
Silicic chloride.		Zincic methide.		Silicic methide.		Zincic chloride.

SILICIC ETHIDE.

$SiEt_4$.

Molecular weight = 144·5. *Molecular volume* ☐☐. 1 *litre of silicic ethide vapour weighs* 72·25 *criths. Boils at* 152°·5.

Preparation.—By the substitution of zincic ethide for zincic methide in the reaction last described, silicic ethide is produced.

Reaction.—Treated with chlorine, one atom of hydrogen is replaced by an atom of chlorine, and *siliconónylic chloride* is formed:—

$$\underset{\text{Silicic ethide.}}{SiEt_3(CMeH_2)} + Cl_2 = \underset{\text{Siliconónylic chloride.}}{\left\{\begin{array}{l} SiEt_3 \\ CMeHCl \end{array}\right.} + HCl.$$

At the same time a portion of the silicic ethide is converted into dichlorinated silicic ethide, which, when heated with aqueous alcohol and potassic acetate, yields disilicic oxyethide,

$$\left\{\begin{array}{l} SiEt_3 \\ O \\ SiEt_3 \end{array}\right. .$$

SILICIC TRIETHOHYDRATE. *Triethyl-silicol.*

$SiEt_3Ho$.

Molecular weight = 132·5. *Molecular volume* □□· 1 *litre of the vapour weighs* 66·25 *criths. Boils at* 153°·5. *Sp. gr. of liquid* 0·8709 *at* 0°.

Preparation.—1. By digesting silicic triethoethylate with water at 200°:—

$$\underset{\substack{\text{Silicic}\\ \text{triethoethylate.}}}{SiEt_3Eto} + OH_2 = \underset{\substack{\text{Silicic}\\ \text{triethohydrate.}}}{SiEt_3Ho} + \underset{\text{Alcohol.}}{OEtH.}$$

2. By the action of aqueous ammonia upon silicic chlortriethide:—

$$\underset{\substack{\text{Silicic}\\ \text{chlortriethide.}}}{SiEt_3Cl} + OH_2 + NH_3 = \underset{\substack{\text{Silicic}\\ \text{triethohydrate.}}}{SiEt_3Ho} + NH_4Cl.$$

SILICOPROPIONIC ACID.

$$\left\{\begin{array}{l} CMeH_2 \\ SiOHo \end{array}\right. .$$

Preparation.—1. This acid, which contains the negative radical SiOHo (that is to say, oxatyl in which carbon is replaced by silicon), is prepared from silicic chlortriethylate by the following series of reactions:—

1st. Silicic chlortriethylate is treated with zincic ethide and sodium, and thus converted into silicic ethotriethylate by the following reaction:—

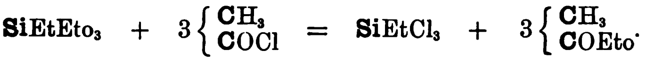
$$\underset{\text{Silicic chlortriethylate.}}{2SiClEto_3} + \underset{\text{Zincic ethide.}}{ZnEt_2} = ZnCl_2 + \underset{\text{Silicic ethotriethylate.}}{2SiEtEto_3}.$$

2nd. Silicic ethotriethylate, which is a colourless liquid, smelling like camphor and boiling at 158°·5, is now heated with concentrated solution of potassic hydrate, when the following change takes place:—

$$\underset{\text{Silicic ethotriethylate.}}{SiEtEto_3} + KHo + OH_2 = \underset{\text{Potassic silicopropionate.}}{SiEtOKo} + \underset{\text{Alcohol.}}{3EtHo}.$$

3rd. From the potassium salt, silicopropionic is obtained by the addition of hydrochloric acid.

2. By heating silicic ethotriethylate with acetylic chloride to 180°, silicic ethotrichloride is produced:—



$$\underset{\text{Silicic ethotriethylate.}}{SiEtEto_3} + \underset{\text{Acetylic chloride.}}{3\left\{\begin{matrix}CH_3\\COCl\end{matrix}\right.} = \underset{\text{Silicic ethotrichloride.}}{SiEtCl_3} + \underset{\text{Ethylic acetate.}}{3\left\{\begin{matrix}CH_3\\COEto\end{matrix}\right.}$$

By the subsequent action of water upon the silicic ethotrichloride, pure silicopropionic acid is obtained as a white insoluble powder resembling silica:—

$$\underset{\text{Silicic ethotrichloride.}}{SiEtCl_3} + 2OH_2 = \underset{\text{Silicopropionic acid.}}{SiEtOHo} + 3HCl.$$

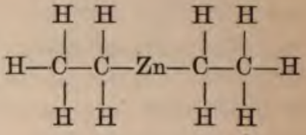
CHAPTER XXXII.

ORGANOMETALLIC BODIES.

THIS term is applied to a family of compounds in which organic radicals are united directly with metals; and it serves to distinguish them from other organic compounds containing metals, in which the metal and organic radical are indirectly united or linked to each other.

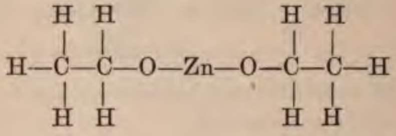
Thus zincic ethide is an organometallic body, while zincic ethylate and zincic succinate are organic bodies containing metals:—

Zincic ethide.. **Zn**Et_2.



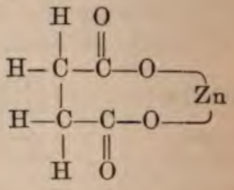
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Zn-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

Zincic ethylate.. **Zn**Eto_2.



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-Zn-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

Zincic succinate.. $\left\{\begin{matrix}\mathbf{C}O\text{—}\\ \mathbf{C}_2H_4\\ \mathbf{C}O\text{—}\end{matrix}\right. Zno''.$



$$\begin{matrix} & H & O & & \\ & | & \| & & \\ H- & C & -C-O- & & \\ & | & & & Zn \\ H- & C & -C-O- & & \\ & | & \| & & \\ & H & O & & \end{matrix}$$

Many organic compounds containing metals are the derivatives of organometallic bodies; thus zincic ethide by oxidation yields zincic ethylate—

$$\underset{\text{Zincic ethide.}}{\mathbf{Zn}Et_2} + O_2 = \underset{\text{Zincic ethylate.}}{\mathbf{Zn}Eto_2};$$

and by further oxidation zincic ethylate can be converted into zincic acetate—

$$\underset{\text{Zincic ethylate.}}{\begin{matrix}\mathbf{C}MeH_2\\ \mathbf{C}MeH_2\end{matrix}Zno''} + 2O_2 = \underset{\text{Zincic acetate.}}{\begin{matrix}\mathbf{C}MeO\\ \mathbf{C}MeO\end{matrix}Zno''} + \underset{\text{Water.}}{2\mathbf{O}H_2}.$$

Another instance of the derivation of organic bodies containing metals from organometallic bodies is seen in the formation of potassic propionate by the action of potassic ethide upon carbonic anhydride :—

$$\underset{\substack{\text{Potassic}\\ \text{ethide.}}}{CMeH_2K} + \underset{\substack{\text{Carbonic}\\ \text{anhydride.}}}{CO_2} = \underset{\substack{\text{Potassic}\\ \text{Propionate.}}}{\left\{\begin{matrix} CMeH_2 \\ COKo \end{matrix}\right.}.$$

Formation of Organometallic Bodies.

Organometallic bodies are produced in a large number of reactions, which may, however, be classed under the following four heads :—

I. By the union of monad positive radicals *in statu nascenti* with a metal, or by the coalescence of a metal with the iodide of a monad positive radical.

Thus, when zinc and ethylic iodide are heated together to 100° in closed vessels, zincic ethide is formed :—

$$\underset{\substack{\text{Ethylic}\\ \text{iodide.}}}{2EtI} + Zn_2 = \underset{\substack{\text{Zincic}\\ \text{ethide.}}}{ZnEt_2} + \underset{\substack{\text{Zincic}\\ \text{iodide.}}}{ZnI_2}.$$

Sometimes light may be employed instead of heat to effect this change, as in the case of the organo-tin compounds. In the formation of organo-mercury compounds by this method, light is indispensable to the reaction :—

$$\underset{\substack{\text{Ethylic}\\ \text{iodide.}}}{EtI} + Hg = \underset{\substack{\text{Mercuric}\\ \text{ethiodide.}}}{HgEtI}.$$

II. By the action of the respective metals alloyed with potassium or sodium upon the iodides or, in rare cases, the bromides of the monad positive radicals.

By this process there is less tendency to form compounds containing both positive radicals and negative elements. Potassium or sodium compounds are never produced in this reaction, because they cannot exist in the presence of ethylic iodide or its homologues. This process is well adapted for the formation of arsenic, antimony, tin, mercury, lead, bismuth, and tellurium compounds :—

$4EtI$	+	$\mathbf{Sn}Na_4$	=	$\mathbf{Sn}Et_4$	+	$4NaI$.
Ethylic iodide.		Tin sodium alloy.		Stannic ethide.		Sodic iodide.

$2EtI$	+	$\mathbf{Hg}Na_2$	=	$\mathbf{Hg}Et_2$	+	$2NaI$.
Ethylic iodide.		Sodium amalgam.		Mercuric ethide.		Sodic iodide.

$2\mathbf{C}_{10}H_7Br$	+	$\mathbf{Hg}Na_2$	=	$\mathbf{Hg}(C_{10}H_7)_2$	+	$2NaBr$.
Naphthylic bromide (bromo-naphthalene).		Sodium amalgam.		Mercuric naphthide.		Sodic bromide.

III. By the action of the zinc compounds of the monad positive radicals upon the haloid compounds, either of the metals themselves, or of their organo- derivatives.

For the production of organometallic bodies containing less positive metals than zinc, this method is generally the most convenient, and is of most universal application. Compounds containing mercury, tin, lead, antimony, and arsenic have been thus produced; but the process has failed when applied to the haloid compounds of copper, silver, platinum, and iron; for, although these bodies are violently acted upon, the organic radicals do not unite with the metal:—

$\mathbf{Sn}Cl_4$	+	$\mathbf{Zn}Et_2$	=	$\mathbf{Sn}Et_2Cl_2$	+	$\mathbf{Zn}Cl_2$.
Stannic chloride.		Zincic ethide.		Stannic dichlorethide.		Zincic chloride.

$\mathbf{Sn}Cl_4$	+	$2\mathbf{Zn}Et_2$	=	$\mathbf{Sn}Et_4$	+	$2\mathbf{Zn}Cl_2$.
Stannic chloride.		Zincic ethide.		Stannic ethide.		Zincic chloride.

$2\mathbf{Hg}EtI$	+	$\mathbf{Zn}Et_2$	=	$2\mathbf{Hg}Et_2$	+	$\mathbf{Zn}I_2$.
Mercuric ethiodide.		Zincic ethide.		Mercuric ethide.		Zincic iodide.

By substituting stannous chloride for stannic chloride in the above reaction, stannic ethide is also obtained, whilst metallic tin is precipitated:—

$2\mathbf{Sn}Cl_2$	+	$4\mathbf{Zn}Et_2$	=	Sn	+	$\mathbf{Sn}Et_4$	+	$4\mathbf{Zn}EtCl$.
Stannous chloride.		Zincic ethide.				Stannic ethide.		Zincic ethochloride.

A precisely similar reaction occurs with plumbic chloride and zincic ethide, plumbic tetrethide being formed:—

$$\underset{\substack{\text{Plumbic}\\\text{chloride.}}}{2PbCl_2} + \underset{\substack{\text{Zincic}\\\text{ethide.}}}{4ZnEt_2} = Pb + \underset{\substack{\text{Plumbic}\\\text{ethide.}}}{PbEt_4} + \underset{\substack{\text{Zincic etho-}\\\text{chloride.}}}{4ZnEtCl}.$$

IV. By the displacement of a metal in an organometallic compound by another and more positive metal.

This method has been successfully employed for the formation of the organo- compounds of potassium, sodium, lithium, aluminium, and zinc. In the first three cases the reaction takes place at ordinary temperatures, some of the original compound entering into the composition of the resulting organometallic body:—

$$\underset{\substack{\text{Zincic}\\\text{ethide.}}}{3ZnEt_2} + Na_2 = \underset{\substack{\text{Sodic zincic}\\\text{ethide.}}}{2ZnNaEt_3} + Zn.$$

$$\underset{\substack{\text{Mercuric}\\\text{ethide.}}}{3HgEt_2} + Al_2 = \underset{\substack{\text{Aluminic}\\\text{ethide.}}}{'Al'''_2Et_6} + 3Hg.$$

$$\underset{\substack{\text{Mercuric}\\\text{amylide.}}}{HgAy_2} + Zn = \underset{\substack{\text{Zincic}\\\text{amylide.}}}{ZnAy_2} + Hg.$$

Reactions of organometallic bodies.

1. The most interesting reaction of the *organo- compounds of the monad metals* is their transformation into salts of normal fatty acids by the action of carbonic anhydride (see p. 146).

2. The *organo- compounds of potassium and sodium* decompose the iodides of the monad positive radicals in the cold, forming hydrides and dyad radicals:—

$$\underset{\substack{\text{Sodic}\\\text{ethide.}}}{C_2H_5Na} + \underset{\substack{\text{Ethylic}\\\text{iodide.}}}{C_2H_5I} = \underset{\substack{\text{Sodic}\\\text{iodide.}}}{NaI} + \underset{\substack{\text{Ethylic}\\\text{hydride.}}}{C_2H_5H} + \underset{\text{Ethylene.}}{C_2H_4}.$$

3. The *organo- compounds of zinc* are decomposed by water, with formation of the hydrides of the radicals:—

$$\underset{\substack{\text{Zincic}\\\text{ethide.}}}{ZnEt_2} + \underset{\text{Water.}}{2OH_2} = \underset{\substack{\text{Zincic}\\\text{hydrate.}}}{ZnHo_2} + \underset{\substack{\text{Ethylic}\\\text{hydride.}}}{2EtH}.$$

4. By the slow action of dry oxygen, they pass through two stages of oxidation:—

$$\underset{\text{Zincic ethide.}}{\mathbf{ZnEt_2}} + O = \underset{\text{Zincic etho-ethylate.}}{\mathbf{ZnEtEto}};$$

$$\underset{\text{Zincic etho-ethylate.}}{\mathbf{ZnEtEto}} + O = \underset{\text{Zincic ethylate.}}{\mathbf{ZnEto_2}}.$$

5. Monad negative elements, such as iodine, remove successively the two atoms of ethyl:—

$$\underset{\text{Zincic ethide.}}{\mathbf{ZnEt_2}} + I_2 = \underset{\text{Zincic ethiodide.}}{\mathbf{ZnEtI}} + \underset{\text{Ethylic iodide.}}{EtI};$$

$$\underset{\text{Zincic ethiodide.}}{\mathbf{ZnEtI}} + I_2 = \underset{\text{Zincic iodide.}}{\mathbf{ZnI_2}} + \underset{\text{Ethylic iodide.}}{EtI}.$$

6. The organo-zinc compounds are extremely useful for the displacement of chlorine or its analogues by ethyl or its homologues:—

$$\underset{\text{Phosphorus trichloride.}}{2\mathbf{P}Cl_3} + \underset{\text{Zincic ethide.}}{3\mathbf{Zn}Et_2} = \underset{\text{Triethyl-phosphine.}}{2\mathbf{P}Et_3} + \underset{\text{Zincic chloride.}}{3\mathbf{Zn}Cl_2}.$$

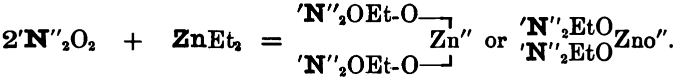
$$\underset{\text{Silicic chloride.}}{\mathbf{Si}Cl_4} + \underset{\text{Zincic ethide.}}{2\mathbf{Zn}Et_2} = \underset{\text{Silicic ethide.}}{\mathbf{Si}Et_4} + \underset{\text{Zincic chloride.}}{2\mathbf{Zn}Cl_2}.$$

$$\underset{\text{Chlorether.}}{2\left\{\begin{matrix}\mathbf{C}_2H_4Cl\\ O\\ \mathbf{C}_2H_4Cl\end{matrix}\right.} + \underset{\text{Zincic ethide.}}{\mathbf{Zn}Et_2} = \underset{\text{Ethylo-chlorether.}}{2\left\{\begin{matrix}\mathbf{C}_2H_4Et\\ O\\ \mathbf{C}_2H_4Cl\end{matrix}\right.} + \underset{\text{Zincic chloride.}}{\mathbf{Zn}Cl_2}.$$

$$\underset{\text{Ethylo-chlorether.}}{2\left\{\begin{matrix}\mathbf{C}_2H_4Et\\ O\\ \mathbf{C}_2H_4Cl\end{matrix}\right.} + \underset{\text{Zincic ethide.}}{\mathbf{Zn}Et_2} = \underset{\text{Diethylated ethylic ether.}}{2\left\{\begin{matrix}\mathbf{C}_2H_4Et\\ O\\ \mathbf{C}_2H_4Et\end{matrix}\right.} + \underset{\text{Zincic chloride.}}{\mathbf{Zn}Cl_2}.$$

Diethylated ethylic ether is isomeric with butylic ether, and contains the radical methylo-ethylated methyl (see p. 8). By oxidation it would doubtless give methylated acetone (p. 221).

7. Oxygen may also be displaced in a similar manner. Thus:—

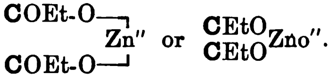


$$2{}'\mathbf{N}''_2O_2 + ZnEt_2 = \begin{array}{l}{}'\mathbf{N}''_2OEt\text{-}O\text{—}\urcorner\\ \qquad\qquad Zn''\\ {}'\mathbf{N}''_2OEt\text{-}O\text{—}\lrcorner\end{array} \text{ or } \begin{array}{l}{}'\mathbf{N}''_2EtO\\ {}'\mathbf{N}''_2EtO\end{array}Zno''.$$

Nitric oxide.	Zincic ethide.	Zincic dinitro-ethylate.

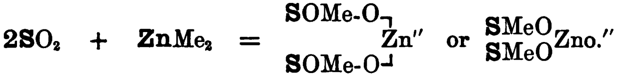
This compound is analogous to zincic propionate, the latter containing two atoms of tetrad carbon in the place of the two tetrad pairs of nitrogen atoms:—

Zincic propionate ....



$$\begin{array}{l}COEt\text{-}O\text{—}\urcorner\\ \qquad\qquad Zn''\\ COEt\text{-}O\text{—}\lrcorner\end{array} \text{ or } \begin{array}{l}CEtO\\ CEtO\end{array}Zno''.$$

8. An analogous reaction is observed with sulphurous anhydride:—



$$2SO_2 + ZnMe_2 = \begin{array}{l}SOMe\text{-}O\urcorner\\ \qquad\quad Zn''\\ SOMe\text{-}O\lrcorner\end{array} \text{ or } \begin{array}{l}SMeO\\ SMeO\end{array}Zno.''$$

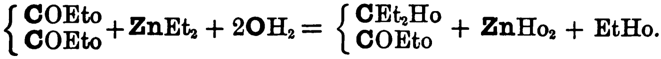
Sulphurous anhydride.	Zincic methide.	Zincic methylsulphinate.

9. When ethylic borate is acted upon by zincic methide, the ethoxyl becomes replaced by methyl:—

$$BEto_3 + 3ZnMe_2 = BMe_3 + 3ZnMeEto.$$

Ethylic borate.	Zincic methide.	Boric methide.	Zincic methide ethylate.

10. When ethylic oxalate is heated with zincic ethide, and water afterwards added, ethylic diethoxalate is formed:—



$$\left\{\begin{array}{l}COEto\\ COEto\end{array}\right. + ZnEt_2 + 2OH_2 = \left\{\begin{array}{l}CEt_2Ho\\ COEto\end{array}\right. + ZnHo_2 + EtHo.$$

Ethylic oxalate.	Zincic ethide.	Water.	Ethylic diethoxalate.	Zincic hydrate.	Alcohol.

11. By the action of ammonia, or of certain amines and amides, zincic ethide exchanges its zinc for hydrogen:—

$$ZnEt_2 + 2NH_3 = ZnAd_2 + 2EtH.$$

Zincic ethide.	Ammonia.	Zincic amide.	Ethylic hydride.

12. The organo-zinc compounds, by losing one semimolecule

of their organic radical, become monad radicals, as shown by the following formulæ:—

Methylozincic dinitromethylate...............	$'\mathbf{N}''_2\mathrm{OMe\text{-}O\text{-}(ZnMe)}$.
Ethylozincic dinitroethylate.................	$'\mathbf{N}''_2\mathrm{OEt\text{-}O\text{-}(ZnEt)}$.
Ethylic ethylo-zincic diethoxalate..........	$\left\{\begin{array}{l}\mathbf{C}\mathrm{Et_2\text{-}O\text{-}(ZnEt)}\\ \mathbf{C}\mathrm{OEto}\end{array}\right.$

13. *Mercuric ethide*, when treated with bromine, loses one-half of its ethyl, which is displaced by the negative element:—

$$\underset{\text{Mercuric ethide.}}{\mathbf{Hg}\mathrm{Et_2}} + \mathrm{Br_2} = \underset{\text{Mercuric ethobromide.}}{\mathbf{Hg}\mathrm{EtBr}} + \underset{\text{Ethylic bromide.}}{\mathrm{EtBr}}.$$

14. *Mercuric methide*, when submitted to the action of mercuric iodide, yields mercuric methiodide:—

$$\underset{\text{Mercuric methide.}}{\mathbf{Hg}\mathrm{Me_2}} + \underset{\text{Mercuric iodide.}}{\mathbf{Hg}\mathrm{I_2}} = \underset{\text{Mercuric methiodide.}}{2\mathbf{Hg}\mathrm{MeI}}.$$

The hydrates corresponding to the mercuric ethobromide and methiodide have been produced. They are powerful caustic bases, of the formulæ

$$\underset{\text{Mercuric ethohydrate.}}{\mathbf{Hg}\mathrm{EtHo}} \text{ and } \underset{\text{Mercuric methohydrate.}}{\mathbf{Hg}\mathrm{MeHo}}.$$

15. The *organo-stannous* compounds unite directly with negative elements, passing into stannic bodies:—

$$\underset{\text{Stannous ethide.}}{\mathbf{Sn}\mathrm{Et_2}} + \mathrm{I_2} = \underset{\text{Stannic iododiethide.}}{\mathbf{Sn}\mathrm{Et_2I_2}}.$$

16. *Hypostannic organo- compounds* undergo a similar transformation:—

$$\underset{\text{Hypostannic ethide.}}{'\mathbf{Sn}'''_2\mathrm{Et_6}} + \mathrm{I_2} = \underset{\text{Stannic iodotriethide.}}{2\mathbf{Sn}\mathrm{Et_3I}}:$$

$$\underset{\text{Stannic iodotriethide.}}{\mathbf{Sn}\mathrm{Et_3I}} + \mathrm{I_2} = \underset{\text{Stannic iododiethide.}}{\mathbf{Sn}\mathrm{Et_2I_2}} + \underset{\text{Ethylic iodide.}}{\mathrm{EtI}}.$$

17. *Hypostannic ethodiniodide* is formed by the action of iodine upon stannic ethodimethide:—

$$\underset{\text{Stannic ethodimethide.}}{2\mathrm{SnEt_2Me_2}} + \mathrm{I_6} = \underset{\text{Hypostannic ethodiniodide.}}{{}'\mathrm{Sn}'''_2\mathrm{Et_4I_2}} + \underset{\text{Methylic iodide.}}{4\mathrm{MeI}}.$$

18. *Stannic ethide*, when treated with hydrochloric acid, yields stannic chlorotriethide and ethylic hydride:—

$$\underset{\text{Stannic ethide.}}{\mathrm{SnEt_4}} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}} = \underset{\text{Stannic chlorotriethide.}}{\mathrm{SnEt_3Cl}} + \underset{\text{Ethylic hydride.}}{\mathrm{EtH}}.$$

The oxide and hydrate corresponding to the stannic chlorotriethide are known; their formulæ are:—

$$\text{Oxide} \;..\; \begin{cases}\mathrm{SnEt_3}\\ \mathrm{O}\\ \mathrm{SnEt_3}\end{cases} ;\ \text{Hydrate}..\ \mathrm{SnEt_3Ho}.$$

These compounds, and the salts which they form, correspond in composition, constitution, and, to a certain extent, in properties, with the compounds of methyl:—

	Alcohol.	Haloid ether.	Ether.
Methylic............	$\mathrm{CH_3Ho}$.	$\mathrm{CH_3Cl}$.	$\begin{cases}\mathrm{CH_3}\\ \mathrm{O}\\ \mathrm{CH_3}\end{cases}$.
Stanntriethylic......	$\mathrm{SnEt_3Ho}$.	$\mathrm{SnEt_3Cl}$.	$\begin{cases}\mathrm{SnEt_3}\\ \mathrm{O}\\ \mathrm{SnEt_3}\end{cases}$.

19. Stannic ethide takes up sulphurous anhydride, at the same time absorbing oxygen from the air, and forms *stanntriethylic ethylsulphonate*:—

$$\underset{\text{Stannic ethide.}}{\mathrm{SnEt_4}} + \underset{\text{Sulphurous anhydride.}}{\mathrm{SO_2}} + \mathrm{O} = \underset{\text{Stanntriethylic ethylsulphonate.}}{\mathrm{SO_2Et(SnEt_3O)}}.$$

20. *Stannic chlorodiethide* is readily reduced to stannous ethide by the action of zinc:—

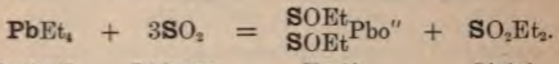
$$\underset{\text{Stannic chlorodiethide.}}{\mathrm{SnEt_2Cl_2}} + \mathrm{Zn} = \underset{\text{Stannous ethide.}}{\mathrm{SnEt_2}} + \underset{\text{Zincic chloride.}}{\mathrm{ZnCl_2}}.$$

21. *Perplumbic ethide* resembles stannic ethide in its reactions; thus with hydrochloric acid it yields perplumbic chlorotriethide and ethylic hydride:—

$$PbEt_4 \quad + \quad HCl \quad = \quad PbEt_3Cl \quad + \quad EtH.$$

Perplumbic ethide. Hydrochloric acid. Perplumbic chlorotriethide. Ethylic hydride.

22. Perplumbic ethide differs, however, from stannic ethide in its action on sulphurous anhydride, with which gas it yields plumbic ethylsulphinate and diethyl sulphone:—



$$PbEt_4 \quad + \quad 3SO_2 \quad = \quad \begin{matrix} SOEt \\ SOEt \end{matrix}Pbo'' \quad + \quad SO_2Et_2.$$

Perplumbic ethide. Sulphurous anhydride. Plumbic ethylsulphinate. Diethyl sulphone.

23. *Perplumbic triethohydrate* ($PbEt_3Ho$) is a powerful base, forming salts with acids.

24. The *organo-tellurium compounds* form oxides and salts. The following are the formulæ of tellurium ethide and some of its compounds:—

Tellurium ethide	$TeEt_2$.
Tellurous diethoxide..........	$TeEt_2O$.
Tellurous diethiodide	$TeEt_2I_2$.
Tellurous diethosulphate	$TeEt_2(S^{vi}O_4)''$.

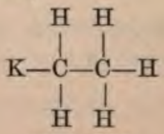
Constitution of Organometallic Bodies.

The organometallic compounds are constituted on the types of the metals they contain. It was, in fact, the study of these bodies which first led to the doctrine of the atomicity of elements. They afford striking examples of monad, dyad, triad, tetrad, pentad, and hexad types.

The organic derivatives of the monad metals are formed on the type of potassic chloride (KCl):—

K—Cl

Potassic chloride.

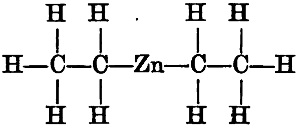


Potassic ethide.

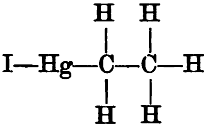
The organo-zinc, cadmium, magnesium, and mercury compounds are formed upon the type of zincic chloride (**Zn**Cl_2):—

$Cl—Zn—Cl$

Zincic chloride.

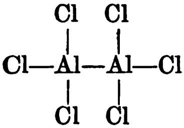


Zincic ethide.

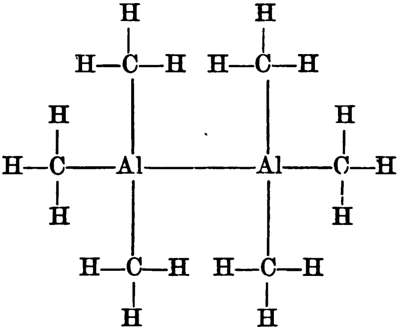


Mercuric iodethide.

The organo-aluminic compounds are formed upon the type of aluminic chloride ('**Al**'''$_2Cl_6$):—

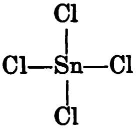


Aluminic chloride.

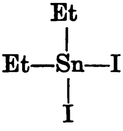


Aluminic methide.

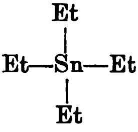
The organo-tin compounds are formed upon the three types ''**Sn**''Cl_2, '**Sn**'''$_2Cl_6$, and **Sn**Cl_4,—the first resembling the zincic chloride type, and the second the aluminic chloride type just described:—



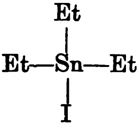
Stannic chloride.



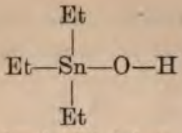
Stannic iododiethide.



Stannic ethide.

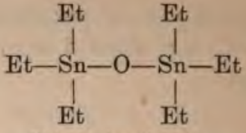


Stannic iodotriethide.



$$\mathrm{Et}-\overset{\mathrm{Et}}{\underset{\mathrm{Et}}{\mathrm{Sn}}}-\mathrm{O}-\mathrm{H}$$

Stannic triethohydrate.



$$\mathrm{Et}-\overset{\mathrm{Et}}{\underset{\mathrm{Et}}{\mathrm{Sn}}}-\mathrm{O}-\overset{\mathrm{Et}}{\underset{\mathrm{Et}}{\mathrm{Sn}}}-\mathrm{Et}$$

Distannic hexethoxide.

The inorganic types of the organo-tellurium series are **Te**Cl_2 and **Te**O_2 :—

$\mathrm{Cl}-\mathrm{Te}-\mathrm{Cl}$

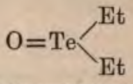
Tellurium chloride.

$\mathrm{O}=\mathrm{Te}=\mathrm{O}$

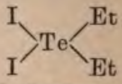
Tellurous oxide.

$\mathrm{Et}-\mathrm{Te}-\mathrm{Et}$

Tellurium ethide.

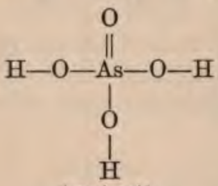


Tellurous diethoxide.



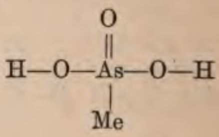
Tellurous diethiodide.

The organo-arsenic, antimony, and bismuth compounds are derived from the types '**As**$''_2$S$''_2$, **As**Cl_3, **As**OHo$_3$, **Sb**Cl_3, **Sb**Cl_5, **Bi**Cl_3, and **Bi**O_2Ho (see pp. 245, 252, and 255):—



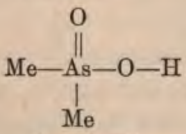
$$\mathrm{H}-\mathrm{O}-\overset{\mathrm{O}}{\underset{\mathrm{OH}}{\mathrm{As}}}-\mathrm{O}-\mathrm{H}$$

Arsenic acid.



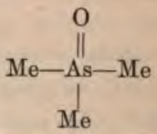
$$\mathrm{H}-\mathrm{O}-\overset{\mathrm{O}}{\underset{\mathrm{Me}}{\mathrm{As}}}-\mathrm{O}-\mathrm{H}$$

Monomethylarsenic acid.



$$\mathrm{Me}-\overset{\mathrm{O}}{\underset{\mathrm{Me}}{\mathrm{As}}}-\mathrm{O}-\mathrm{H}$$

Cacodylic acid.



$$\mathrm{Me}-\overset{\mathrm{O}}{\underset{\mathrm{Me}}{\mathrm{As}}}-\mathrm{Me}$$

Arsenic oxytrimethide.

The effect of the substitution of positive for negative radicals in compounds is strikingly exhibited in the case of arsenic acid, **As**OHo$_3$, as illustrated in the above graphic representations. By the substitution of one semimolecule of methyl for hydroxyl, a well-defined acid (less negative, however, than arsenic acid) is produced, monomethylarsenic acid, $AsOMeHo_2$. By the replacement of a second semimolecule of hydroxyl by methyl, a very feeble acid, cacodylic acid, $AsOMe_2Ho$, is obtained. By the replacement of the third semimolecule of hydroxyl by methyl, the acid properties are completely destroyed, a feeble base, the arsenic oxytrimethide, being formed, $AsOMe_3$. Finally, by the substitution of methyl and hydroxyl for the remaining atom of oxygen, there is produced a powerful base, tetramethylarsonic hydrate, $AsMe_4Ho$.

The following is a list of the principal organometallic bodies at present known:—

I. Organo- compounds containing monad metals:—

Potassio-zincic methide	$KMe,ZnMe_2$.
Potassio-zincic ethide	$KEt,ZnEt_2$.
Sodio-zincic ethide	$NaEt,ZnEt_2$.
Lithio-zincic ethide	$LiEt,ZnEt_2$.
Lithio-mercuric ethide	$LiEt,HgEt_2$.

II. Organo- compounds containing dyad metals:—

Magnesic ethide	$MgEt_2$.
Zincic methide	$ZnMe_2$.
Zincic ethide	$ZnEt_2$.
Zincic amylide	$ZnAy_2$.
Mercuric methide	$HgMe_2$.
Mercuric ethide	$HgEt_2$.
Mercuric methiodide	$HgMeI$.
Mercuric ethonitrate	$HgEt(NO_3)$.
Stannous ethide	$''Sn''Et_2$.
Tellurium methide	$TeMe_2$.

III. Organo- compounds containing triad metals:—

These compounds belong to the [illegible] family of organic bodies, and have been treated of at p. [illegible]

IV. Organo- compounds of tetrad metals:—

Stannic methide	SnMe_4.
Stannic iodotrimethide..........	$\mathrm{SnMe}_3\mathrm{I}$.
Stannic iododimethide	$\mathrm{SnMe}_2\mathrm{I}_2$.
Hypostannic ethide	$'\mathrm{Sn}'''_2\mathrm{Et}_6$.
Stannic ethylodimethide	$\mathrm{SnEt}_2\mathrm{Me}_2$.
Stannic phenyl-triethide	SnPhEt_3.
Stannic ethophenyl-dichloride....	$\mathrm{SnPhEtCl}_2$.
Hypostannic ethodiiodide	$'\mathrm{Sn}'''_2\mathrm{Et}_4\mathrm{I}_2$.
Perplumbic ethide	PbEt_4.
Perplumbic chlorotriethide	$\mathrm{PbEt}_3\mathrm{Cl}$.

V. Organo- compounds of pentad metals :—

These bodies belong to the 11th family of organic compounds, and have been already treated of at pp. 251 and 25

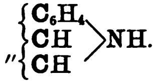
APPENDIX TO CHAPTER XXIX.

COMPOUNDS CONTAINING TRIAD NITROGEN.

THE INDIGO GROUP.

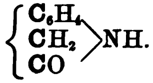
THIS group of compounds, of which the most important is *indigotin*, C_8H_5NO, the blue colouring matter of indigo, may be regarded as derived from *indole*, C_8H_7N. The following list of the principal members of the group, with their constitutional formulæ, will render clear the nature of this relationship :—

Indole ....



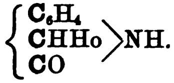
$$''\left\{\begin{array}{l}C_6H_4\\CH\\CH\end{array}\right\rangle NH.$$

Oxindole ....



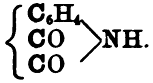
$$\left\{\begin{array}{l}C_6H_4\\CH_2\\CO\end{array}\right\rangle NH.$$

Dioxindole ....



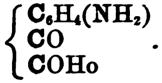
$$\left\{\begin{array}{l}C_6H_4\\CHHo\\CO\end{array}\right\rangle NH.$$

Isatin ....



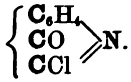
$$\left\{\begin{array}{l}C_6H_4\\CO\\CO\end{array}\right\rangle NH.$$

Isatic acid ....



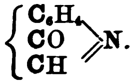
$$\left\{\begin{array}{l}C_6H_4(NH_2)\\CO\\COHo\end{array}\right. .$$

Isatic chloride ....



$$\left\{\begin{array}{l}C_6H_4\\CO\\CCl\end{array}\right\rangle N.$$

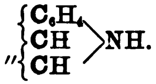
Indigotin ....



$$\left\{\begin{array}{l}C_6H_4\\CO\\CH\end{array}\right\rangle N.$$

All the above compounds are ortho-disubstitution derivatives of benzene, and all, with the exception of isatic acid, contain closed lateral chains (see p. 45).

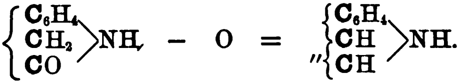
INDOLE.



$$''\left\{\begin{matrix}C_6H_4\\CH\\CH\end{matrix}\right\rangle NH.$$

Molecular weight = 117. *Molecular volume* □□. 1 *litre of indole vapour weighs* 58·5 *criths. Fuses at* 52°. *Boils at* 245°.

Preparation.—1. By the distillation of oxindole (p. 281) with zinc-dust:—

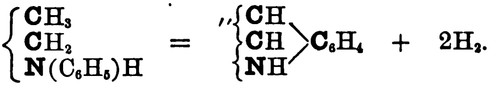


$$\left\{\begin{matrix}C_6H_4\\CH_2\\CO\end{matrix}\right\rangle NH - O = ''\left\{\begin{matrix}C_6H_4\\CH\\CH\end{matrix}\right\rangle NH.$$

Oxindole. Indole.

2. By digesting albumen with pancreas.

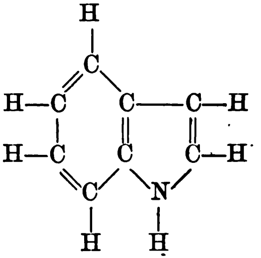
3. By passing the vapour of ethylaniline or of ortho-diethyltoluidine through a red-hot tube:—



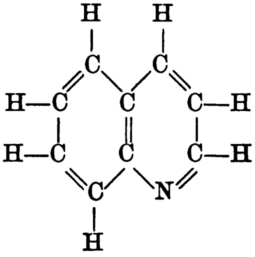
$$\left\{\begin{matrix}CH_3\\CH_2\\N(C_6H_5)H\end{matrix}\right. = {}''\left\{\begin{matrix}CH\\CH\\NH\end{matrix}\right\rangle C_6H_4 + 2H_2.$$

Ethylaniline. Indole.

This reaction is analogous to that in which quinoline is formed from acrolein-aniline (p. 233). The relation of indole to quinoline will be seen by comparing the graphic formulæ of the two compounds:—

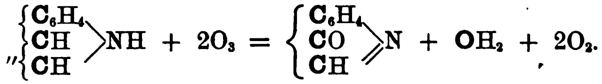


Indole.



Quinoline.

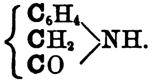
Reaction.—By oxidation with ozone, indole yields traces of indigotin:—



$$\left\{\begin{array}{l}C_6H_4\\CH\\CH\end{array}\right\rangle NH + 2O_3 = \left\{\begin{array}{l}C_6H_4\\CO\\CH\end{array}\right\rangle N + OH_2 + 2O_2.$$

Indole. Ozone. Indigotin. Water.

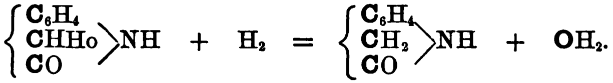
OXINDOLE.



$$\left\{\begin{array}{l}C_6H_4\\CH_2\\CO\end{array}\right\rangle NH.$$

Fuses at 120°.

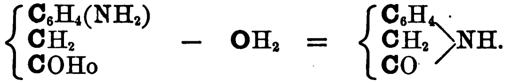
Preparation.—1. By the reduction of dioxindole (see below) with tin and hydrochloric acid:—



$$\left\{\begin{array}{l}C_6H_4\\CHHo\\CO\end{array}\right\rangle NH + H_2 = \left\{\begin{array}{l}C_6H_4\\CH_2\\CO\end{array}\right\rangle NH + OH_2.$$

Dioxindole. Oxindole.

2. When ortho-nitrophenylacetic acid is subjected to the action of reducing agents, ortho-amidophenylacetic acid is formed, and this, at the moment of formation, parts with the elements of water, yielding oxindole:—

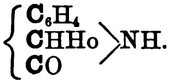


$$\left\{\begin{array}{l}C_6H_4(NH_2)\\CH_2\\COHo\end{array}\right. - OH_2 = \left\{\begin{array}{l}C_6H_4\\CH_2\\CO\end{array}\right\rangle NH.$$

Ortho-amidophenylacetic acid. Water. Oxindole.

Oxindole is thus the *internal alkalamide* of orthoamidophenylacetic acid.

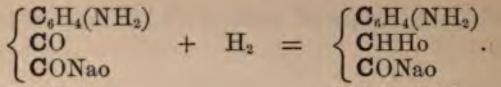
DIOXINDOLE.



$$\left\{\begin{array}{l}C_6H_4\\CHHo\\CO\end{array}\right\rangle NH.$$

Fuses at 180°.

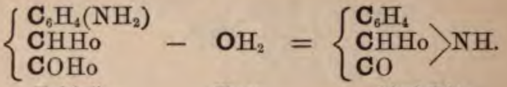
Preparation.—By the action of sodium amalgam upon sodic isatate (p. 283), sodic hydrindate is formed:—



$$\left\{\begin{array}{l}\mathbf{C}_6H_4(NH_2)\\ \mathbf{C}O\\ \mathbf{C}ONao\end{array}\right. + H_2 = \left\{\begin{array}{l}\mathbf{C}_6H_4(NH_2)\\ \mathbf{C}HHo\\ \mathbf{C}ONao\end{array}\right. .$$

Sodic isatate. Sodic hydrindate. (Ortho-amidophenylglycollate, p. 188.)

Hydrindic acid cannot exist in the free state, but, when liberated from its salts by a stronger acid, parts with the elements of water, forming dioxindole :—

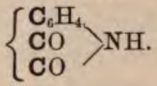


$$\left\{\begin{array}{l}\mathbf{C}_6H_4(NH_2)\\ \mathbf{C}HHo\\ \mathbf{C}OHo\end{array}\right. - \mathbf{O}H_2 = \left\{\begin{array}{l}\mathbf{C}_6H_4\\ \mathbf{C}HHo\\ \mathbf{C}O\end{array}\right\rangle NH.$$

Hydrindic acid. Water. Dioxindole.

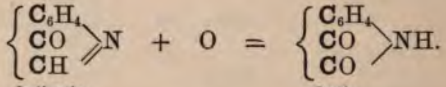
Dioxindole is the internal alkalamide of hydrindic (ortho-amidophenylglycollic) acid.

ISATIN.



$$\left\{\begin{array}{l}\mathbf{C}_6H_4\\ \mathbf{C}O\\ \mathbf{C}O\end{array}\right\rangle NH.$$

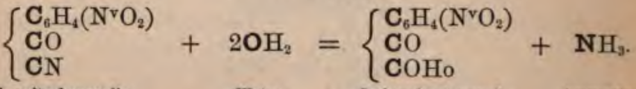
Preparation.—1. By the oxidation of indigo with nitric acid :—



$$\left\{\begin{array}{l}\mathbf{C}_6H_4\\ \mathbf{C}O\\ \mathbf{C}H\end{array}\right\rangle N + O = \left\{\begin{array}{l}\mathbf{C}_6H_4\\ \mathbf{C}O\\ \mathbf{C}O\end{array}\right\rangle NH.$$

Indigotin. Isatin.

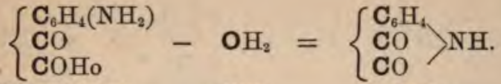
2. By treating ortho-nitrobenzoylic cyanide with aqueous hydrochloric acid, the cyanogen group is converted into oxatyl, yielding ortho-nitrobenzoylformic acid :—



$$\left\{\begin{array}{l}\mathbf{C}_6H_4(N^vO_2)\\ \mathbf{C}O\\ \mathbf{C}N\end{array}\right. + 2\mathbf{O}H_2 = \left\{\begin{array}{l}\mathbf{C}_6H_4(N^vO_2)\\ \mathbf{C}O\\ \mathbf{C}OHo\end{array}\right. + \mathbf{N}H_3.$$

Ortho-nitrobenzoylic cyanide. Water. Ortho-nitrobenzoyl-formic acid. Ammonia.

By the reduction of this nitro-acid, the corresponding amido-acid is obtained. The amido-acid, however, cannot exist in the free state, but parts with the elements of water, yielding isatin :—

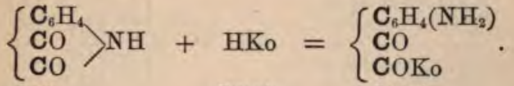


$$\left\{\begin{matrix} C_6H_4(NH_2) \\ CO \\ COHo \end{matrix}\right. - OH_2 = \left\{\begin{matrix} C_6H_4 \\ CO \\ CO \end{matrix}\right\rangle NH.$$

Ortho-amidobenzoyl-formic (isatic) acid. Water. Isatin.

Isatin is thus the internal alkalamide of ortho-amidobenzoylformic (isatic) acid, an acid of the benzene-pyruvic series (see p. 182).

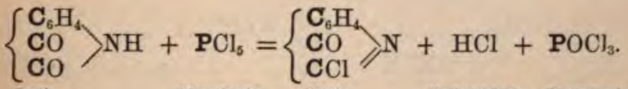
Reactions.—1. Boiled with a solution of an alkaline hydrate, isatin yields a salt of isatic acid :—



$$\left\{\begin{matrix} C_6H_4 \\ CO \\ CO \end{matrix}\right\rangle NH + HKo = \left\{\begin{matrix} C_6H_4(NH_2) \\ CO \\ COKo \end{matrix}\right. .$$

Isatin. Potassic hydrate. Potassic isatate.

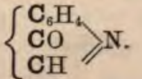
2. By the action of phosphoric chloride isatic chloride is formed :—



$$\left\{\begin{matrix} C_6H_4 \\ CO \\ CO \end{matrix}\right\rangle NH + PCl_5 = \left\{\begin{matrix} C_6H_4 \\ CO \\ CCl \end{matrix}\right\rangle N + HCl + POCl_3.$$

Isatin. Phosphoric chloride. Isatic chloride. Hydrochloric acid. Phosphoric oxytrichloride.

INDIGOTIN.



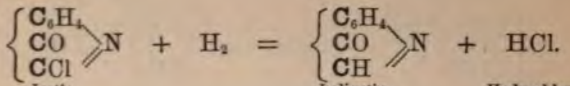
$$\left\{\begin{matrix} C_6H_4 \\ CO \\ CH \end{matrix}\right\rangle N.$$

Occurrence.—This compound, the blue colouring matter of indigo, is obtained from various species of *indigofera.* The substance which occurs in the plants is, however, not indigotin, but *indican,* from which, by the action of ferments, indigotin is produced :—

$$\underset{\text{Indican.}}{C_{26}H_{31}NO_{17}} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Indigotin.}}{C_8H_5NO} + \underset{\text{Indiglucin.}}{3C_6H_{10}O_6}.$$

Boiling with acids decomposes indican in the same way.

Preparation.—1. By the action of hydrogenating agents on isatic chloride:—

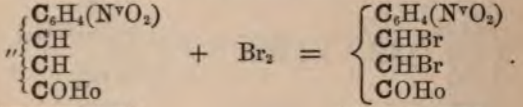


$$\left\{\begin{array}{l}C_6H_4\\CO\\CCl\end{array}\right. \!\!> N + H_2 = \left\{\begin{array}{l}C_6H_4\\CO\\CH\end{array}\right. \!\!> N + HCl.$$

Isatic chloride. Indigotin. Hydrochloric acid.

2. Indigotin is at present prepared on a large scale from ortho-nitrocinnamic acid by the following series of reactions:—

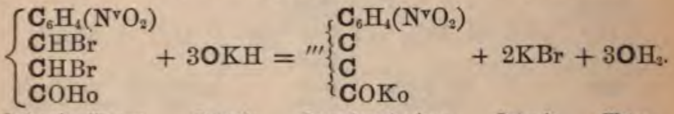
By direct union of ortho-nitrocinnamic acid with bromine, ortho-nitrodibromohydrocinnamic acid is obtained:—



$$''\left\{\begin{array}{l}C_6H_4(N^vO_2)\\CH\\CH\\COHo\end{array}\right. + Br_2 = \left\{\begin{array}{l}C_6H_4(N^vO_2)\\CHBr\\CHBr\\COHo\end{array}\right. .$$

Ortho-nitrocinnamic acid. Ortho-nitrodibromohydrocinnamic acid.

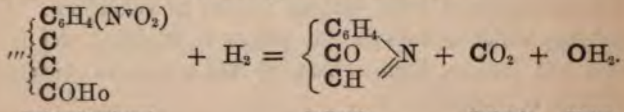
By the action of potassic hydrate upon this bromo-acid, the potash salt of ortho-nitrophenylpropiolic acid is produced:—



$$\left\{\begin{array}{l}C_6H_4(N^vO_2)\\CHBr\\CHBr\\COHo\end{array}\right. + 3OKH = '''\left\{\begin{array}{l}C_6H_4(N^vO_2)\\C\\C\\COKo\end{array}\right. + 2KBr + 3OH_2.$$

Ortho-nitrodibromohydrocinnamic acid. Potassic hydrate. Potassic orthonitrophenylpropiolate. Potassic bromide. Water.

When ortho-nitrophenylpropiolic acid is reduced with grape-sugar in alkaline solution, indigotin is formed, carbonic anhydride being evolved during the process. The mechanism of the reaction is not perfectly understood, but the change probably takes place as follows:—



$$'''\left\{\begin{array}{l}C_6H_4(N^vO_2)\\C\\C\\COHo\end{array}\right. + H_2 = \left\{\begin{array}{l}C_6H_4\\CO\\CH\end{array}\right. \!\!> N + CO_2 + OH_2.$$

Ortho-nitrophenylpropiolic acid. Indigotin. Carbonic anhydride. Water.

The indigotin obtained by these processes is identical with the natural product.

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